

✓ **FABRICATION OF AN EXPERIMENTAL SET-UP
FOR MEASUREMENT OF SECOND VIRIAL COEFFICIENTS**

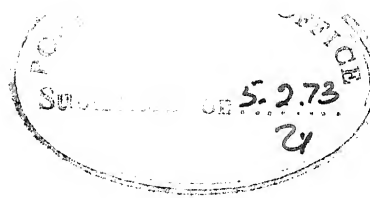
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for the Degree of
MASTER OF TECHNOLOGY

By
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to the

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FEBRUARY 1973



(ii)

CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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CHAPTER I.

INTRODUCTION

Evaluation of thermodynamic properties of a pure gas or gaseous mixture needs the knowledge of pressure-volume-temperature behaviour of the substance. This knowledge may be available in the form of experimental P-V-T data or as an appropriate equation of state inter-relating the macroscopic properties like pressure, specific volume, and temperature. There are many equations of state¹ like van der Waal's equation of state, Benedict-Webb-Rubin equation of state, Berthelot equation of state, Redlich-Kwang equation of state, Martin-Hau equation of state etc. Most of these equations of state are empirical in nature and the constants in the equations do not have any physical significance. The equation which has a sound theoretical basis, and can be extended to mixtures without much empiricism is the virial equation of state.

All real gases exhibit deviations from ideal behaviour because of the existence of intermolecular forces, and the constants in the virial equation of state, namely the virial coefficients, depict the intermolecular interactions between the like and the unlike molecules. For example, the second, third, and fourth virial coefficients represent the non-ideality introduced in the gas due to binary, ternary and quaternary intermolecular interactions respectively.

Statistical mechanical methods provide theoretical relationships for calculating the virial coefficients from a knowledge of the intermolecular forces available in the form of potential models. Experimental data on the virial coefficients can be used for testing the validity of these methods. Since the virial coefficients give a measure of nonideality of a system, they can in turn be used for estimating other properties revealing nonideality such as the excess functions and critical temperature. The usefulness of the virial equation of state lies not only in estimating thermodynamic properties but also in calculating transport properties such as viscosity, diffusivity, etc. because, the virial coefficients are directly related to the fundamental property of molecules, namely the intermolecular forces.

Determination of the constants in any equation of state comprises measurement of P-V-T data of the particular substance and fitting the data into the required equation of state for evaluating the constants.

A few experimental methods are available for determination of these virial coefficients, such as the NMR technique², the chromatographic technique³, the direct measurement of Pressure-Volume-Temperature of the gas etc.

Experimental set-ups developed for determination of the virial coefficients vary in elaborateness and efficiency. The most sophisticated set-up is due to

McGlashan and Potter⁴ who used a differential method.

In this method the substance under investigation is compared with a reference (standard) substance whose properties are known and consequently this eliminates any standard error in the measurement. This technique is an improved version of the original work of Addingly and Withlaw Gray⁵. The apparatus is very complicated and tedious to construct. Another well-established method is due to Burnet⁶. This method involves repeated expansion of the substance under investigation and requires the measurement of temperature and pressure only.

All the above methods have limitations in pressure and temperature. The apparatus in which one can work much above the critical point, and is relatively simple to fabricate, and is versatile in design and operation, was used for the present work. The same apparatus can be used for multicomponent vapour-liquid equilibria by the static method in which a sample of known composition is subjected to a constant temperature and the bubble point and dew point pressures are measured. The set-up was originally designed by Kay⁷ in 1928 for multicomponent vapour-liquid equilibrium studies. Since then it has undergone several modifications.

The present work comprises fabrication of the set-up with necessary modifications and its standardization. It is further intended to measure the P-V-T data for determination

of the second virial coefficients of Monochlorobenzene in order to show the versatility of the apparatus. The fabrication work includes setting up of a vacuum loading train for degassing and loading of the sample under investigation.

CHAPTER II

EXPERIMENTAL SET-UP AND PROCEDURE

The experimentation basically involves measurement of pressure, specific volume and temperature of a pure substance in gaseous phase. According to Gibbs phase rule, the system has two degrees of freedom and so two properties can be varied independently. In the present work a sample of known mass is maintained at a constant temperature, thus fixing one property, and the other property, pressure is varied over a range. The corresponding volumes occupied by the sample are measured along with temperature and pressure.

METHOD:

Experimental set-up is similar to the one designed by Kay for measurement of phase equilibria by the static method. Slight modifications have been incorporated to satisfy the needs of the present work and availability of materials of construction. A brief outline of the method involved will be given first, the detailed description of the apparatus and procedure will then follow.

The schematic diagram of the set-up is given in Figure 1. The principal part of the set-up is an experimental tube (ET) which contains the sample under investigation at its top. It is a precision bored glass capillary

FIG. 1 - EXPERIMENTAL SET-UP.

with one end closed and the other having a 10/30 ground glass joint. The experimental tube is surrounded by a double walled vapour jacket (VJ) which acts as a constant temperature bath. The tube is held vertical with closed end upwards from one cylinder (A) of a U-shaped unit called compressor block (A,B,C). Pure air free mercury acts as a pressure transmitting medium in the compressor block and hence fills up the compressor block and part of the experimental tube. Sample under investigation is confined over mercury in the experimental tube. The other cylinder (B) of the compressor block is connected to a high pressure nitrogen cylinder (N¹) with a regulator via a manifold (MF) to exert requisite pressure on the sample in experimental tube. The exact pressure of the sample is obtained after making necessary connections to the nitrogen pressure in the manifold which is read by means of a precision Bourdan gauge (PB). Changes in the volume of the sample are affected by either introducing mercury into or withdrawing mercury from the experimental tube via compressor block to a mercury storage unit called mercury displacer (MD). This unit is connected to the cylinder (B) of the compressor block. Volume of the sample is obtained from the prior calibration chart after measuring the distance between closed tip and mercury level in the experimental tube. Distances are measured by means of a Gaertner cathetometer which can read heights as small as 0.0001 cm. Temperature of the

sample which is the same as the temperature inside the vapour jacket is measured by means of a copper-constantan thermocouple dipped into the thermowell of vapour jacket(VJ). Honeywell potentiometer is used to measure the voltage developed in the thermocouple. A small steel ball is provided in the experimental tube along with the sample to provide agitation of the sample so that equilibrium is easily attained in the system. The ball is moved up and down several times by means of a permanent horse-shoe magnet which is held firmly by hand and moved around the vapour jacket. Attainment of equilibrium is ensured by observing constancy of volume reading over a period of time provided temperature and pressure of the system are maintained constant.

Before any measurement is made, it is necessary to degas the sample to remove air and any other noncondensable gases that may be absorbed in the sample. Presence of these gases in the sample will result in positive deviations in pressure, that is, the observed pressure will be more than what it should be for a pure substance devoid of air and other noncondensable gases, at the same temperature and specific volume. As a result, instead of sharp changes in the slopes of the isotherms of liquid (single phase) and liquid + vapour (2-phase), a continuous curved isotherm is observed around the saturation points, the reason being the total pressure is the sum of the true vapour-pressure

of the pure substance and the partial pressures of air and other non-condensables.

Degassing of the sample and subsequent loading of the experimental tube with the degassed sample are performed under high vacuum in a specially designed and fabricated all glass unit named the Vacuum Loading Train. Degassing of the sample is done by a series of operations which involves freezing of the liquid sample with dry-ice + acetone mixture and pumping off the residual gas over the frozen substance to a high vacuum (10^{-5} mm of Hg) followed by melting and distillation at low pressures. Before the loaded experimental tube is detached from the vacuum Loading Train, the former is completely filled with degassed mercury while keeping the sample in frozen condition so that the degassed sample is kept isolated from the surroundings until it is fixed to the cylinder (A) of compressor block.

DESCRIPTION OF THE APPARATUS:

(a) Vacuum Loading Train:

The schematic diagram of the vacuum loading train is given in Figure 2. It consists of a long glass manifold (M1) to which all component parts are connected. A mercury manometer (M2) at the extreme left end indicates the approximate magnitude of the vacuum upto 1 mm of Hg. in the system. F1, F2, F3, F4, and F5 are 250 cc capacity flasks, which serve as reservoirs for the distillation of

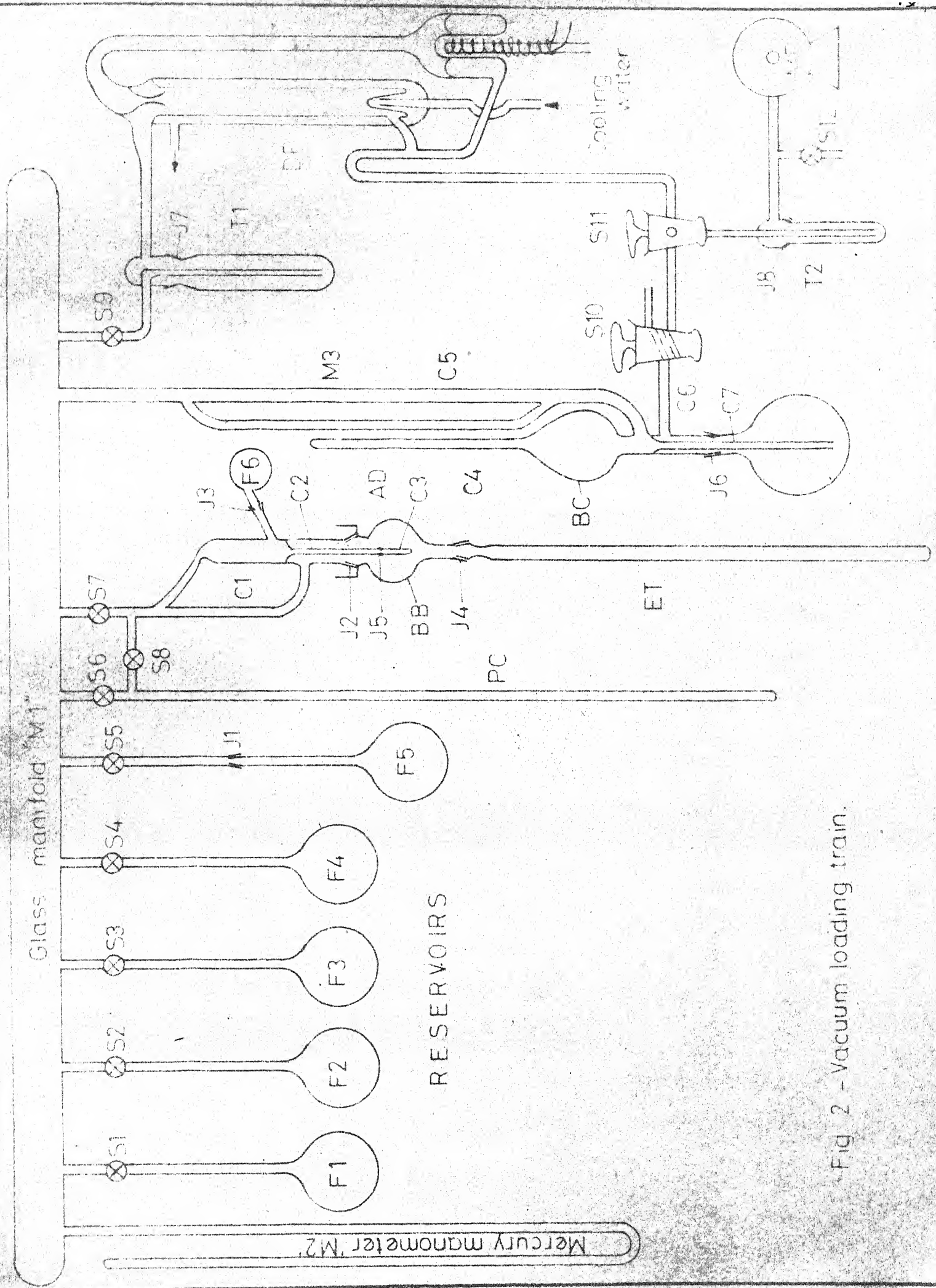


Fig 2 - Vacuum loading train.

sample, are attached to the manifold (M1) via L-shaped high vacuum stop cocks, S1, S2, S3, S4, and S5 respectively. The flask (F5), which has a ground glass joint (J1), is removable from the Loading Train. Sample is initially charged into this flask and later transferred to one of the flasks, F1, F2, F3, F4. The joint (J1) is not greased. A mercury cup is made to keep this joint vacuum tight as follows. A hole is drilled on a rubber stopper and a piece of glass tubing is inserted around it. The removable flask passes through the drilled hole and is fixed to the joint (J1). Thus the glass tube forms a cup around the joint. Sufficient amount of mercury is poured into the cup so that the joint is completely surrounded by mercury which forms a mercury sealing. This type of sealing stands vacuum as high as 10^{-6} mm of Hg. Degassing of the sample is done by repeated distillation of the substance under high vacuum between two flasks. Two flasks are then sufficient to degas one pure component. But more number of flasks are inserted so as to degas three samples at one loading and load the experimental tube with them for multicomponent vapour-liquid equilibrium studies. PC is a calibrated precision bored glass tube with stop cock (S6) separating it from the manifold. This should be attached exactly vertical. The quantity of the sample to be loaded is measured in this before transferring it into the experimental tube after degassing. By the side of

this tube there is a unit (C1) which is connected to the manifold via the stop cock (S8). The experimental tube is vertically held to this unit via an adaptor (AD). C1 has a glass joint (J2) at its bottom to which fits the adaptor (AD) with a mercury cup around the joint. Side arm of C1 is slightly inclined upwards with a glass joint (J3) which holds a 100 cc flask (F6) with inclined neck. Mercury, with which degassed sample is to be sealed in the experimental tube after loading, is taken into this flask. The adaptor (AD) has a blown bulb (BB) and a 10/30 ground glass joint (J4) near its bottom. The experimental tube is held to this with the help of a 10/30 joint (J4). This joint also cannot be greased and mercury sealing is used. The unit (C1) has glass tube (C2) with a glass joint (J5) at its bottom, which extends from below the side arm through the joint (J2) upto the middle of the blown bulb (BB) of the adaptor (AD). Another small tube (C3) with one end drawn to form a nozzle and a joint (J5) at the other end fits into the tube (C2). This will allow the mercury from the flask (F6), when tilted, to fall dropwise into the experimental tube. When the drop leaves the nozzle of C3 near the end of blown bulb (BB), mercury expands and any entrapped air in it is removed into the liquid nitrogen trap (T1) by the diffusion pump (DP). There is a way between PC and C1 with a stop cock (S7) in it, so as to by pass the manifold when transferring the

measured sample from PC to the experimental tube. For indication of high vacuum in the system a McLeod gauge (M3) is attached to the manifold (M1) by the side of the unit (C1). M3 consists of a 250 cc flask (F7) at its bottom with a glass joint (J6), a bulb (BC), a glass capillary (C4) above the bulb (BC), a comparison capillary (C5), a side tube (C6) slightly above the joint (J6), a central tube (C7) extending from slightly above the side tube (C6) upto the bottom of the flask (F7). The side tube is connected to the one-limb side of a three-way oblique bored stop cock (S10). One of its parallel limbs on the other side is left open to atmosphere and the other is connected to one side limb of a three way T-shaped stop cock (S11). The manifold (M1) has a way to the stop cock (S10) through McLeod gauge (M3) only through the tube (C7). When the flask (F7) is filled up with mercury, this way is cut off. The flask (F7) is to be charged with enough (about 220 cc) of mercury so that a column of 76 cm of mercury can be raised above the level of mercury left in F7, filling up the bulb (BC) and capillaries (C4) and (C5). The bottom limb of the stop cock (S11) is connected to a mechanical pump (MP) through an ice trap (T2) with a glass joint (J8). Between the pump (MP) and trap (T2) a stop cock (S12) is connected side way with one limb open to atmosphere for venting the pump (MP) when it is shut off after operation. The other side limb of stop cock (S11) is connected to the

mercury diffusion pump (DP). DP is also connected to the one end of the manifold (M1) through a liquid nitrogen Trap (T1) with glass joint (J7) and a L-shaped stop cock (S9). During any transfer of the sample in the loading train the diffusion pump (DP) should be disconnected from the system by closing the stop cock (S9). The liquid nitrogen trap (T1) does not allow any noncondensable gases and air to diffuse into the diffusion pump (DP) as they are made to condense in the trap (T1) at the liquid nitrogen temperature. Similarly the ice trap (T2) does not allow any vapour to pass into the oil of the mechanical pump (MP). Contamination of oil and mercury in the mechanical and diffusion pumps respectively reduces their efficiencies. Diffusion pump (DP) requires about 50 cc of mercury. The diffusion pump should always be kept under vacuum in order to avoid any oxidation of mercury in presence of atmospheric air. Heating of mercury in DP is provided by 22-gauge heating wire of two meters length wound on a porecelain rod and inserting into the well inside the mercury reservoir. Power to the heating wire is supplied from 220V mains through a variac. The mercury vapour generated in the reboiler of the diffusion pump passes through a nozzle creating high suction. Later it is condensed with the help of tap water and returned to the reboiler through a separate line. The pump is sufficiently insulated with glass-wool for avoiding unnecessary heat loss to the surroundings.

(b) P-V-T Apparatus:

The apparatus in which actual P-V-T measurement on the substance is carried out comprises two units; namely (i) a pressure system which is all metal apparatus except for the experimental tube; (ii) a vacuum system which is all glass unit.

(i) Pressure System: This consists of experimental tube (ET), compressor block (A,B,C), Mercury displacer (MD), Manifold (MF), Precision Bourdan gauge (PB), Ordinary pressure gauge (PG), Accumulator (AC), Nitrogen Cylinder (N1) with high pressure regulator etc. These component parts are separately discussed below:

Experimental Tube: This is made of precision bored thick walled glass tubes of two different sizes. The detailed drawing with exact dimensions is given in Figure 3. One of its ends is sealed and the other has a 10/30 glass joint (J4) to fit to the adaptor (AD) of the vacuum loading train. This is held vertical with its closed end upwards from the cylinder (A) of the compressor block by means of a specially designed packing gland (P). The sample is confined over mercury in it. It is calibrated prior to use in the set-up for the exact volume from closed tip to any level in the tube as a function of the distance between the outside of closed tip to the same level. The details of calibration are given in Appendix A.

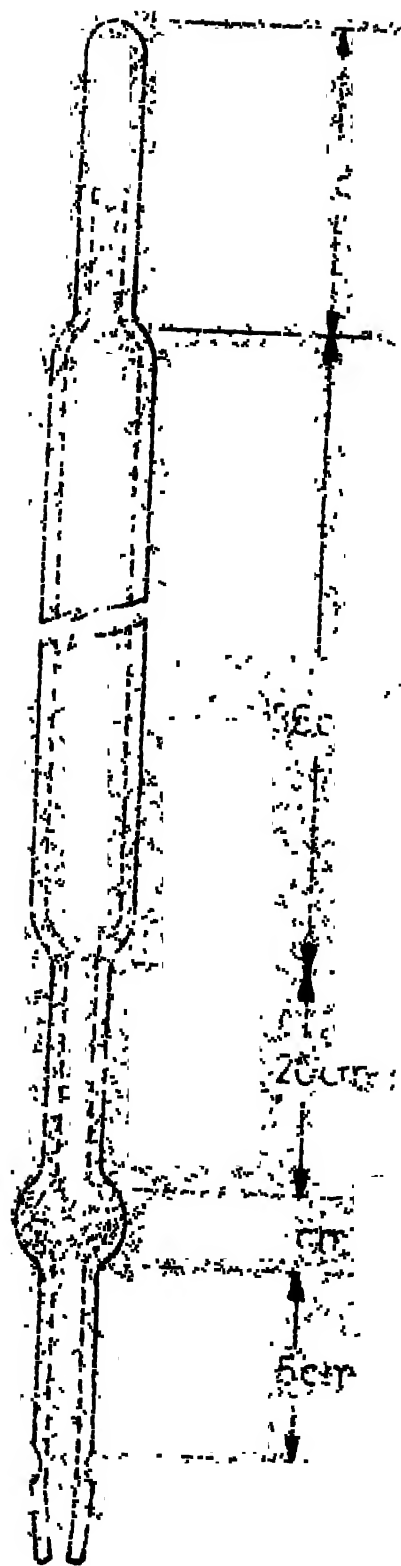


Fig. 3 - Experiment 11 - W.P.

Compressor Block: This is a U-shaped unit consisting of two hollow upright cylinders (A) and (B) which are connected at the bottom via a check valve (C). The sketch of the assembly is shown in Figure 4. C is inclined upwards to the right at an angle of 30° from the horizontal. The cylinder (A) holds the experimental tube (ET) vertically with its closed end upwards while pressure is exerted on the sample. A specially designed packing gland (P) is used to hold the experimental tube firmly from the cylinder (A) without exerting any local strain at any position on the glass, but at the same time providing a leak-proof fitting between the glass and the metal. The purpose of the compressor block is two fold: (i) To provide a continuous path of mercury from cylinder (B) to the experimental tube, and so the pressure exerted on the mercury in the cylinder (B) by high pressure nitrogen gas is transmitted to the sample in the experimental tube; (ii) to affect changes in volume of the sample in the experimental tube by withdrawing or introducing mercury from or to the experimental tube.

Check valve (C) is to prevent the spilling of mercury all over in case the experimental tube breaks while operating at high pressures. A steel ball of proper size is provided inside C which can freely move in C but big enough not to enter the cylinder (A) and (B) through side limbs of A and B. This ball floats in mercury and so will rest to the right extreme end of C under normal operating conditions. If the

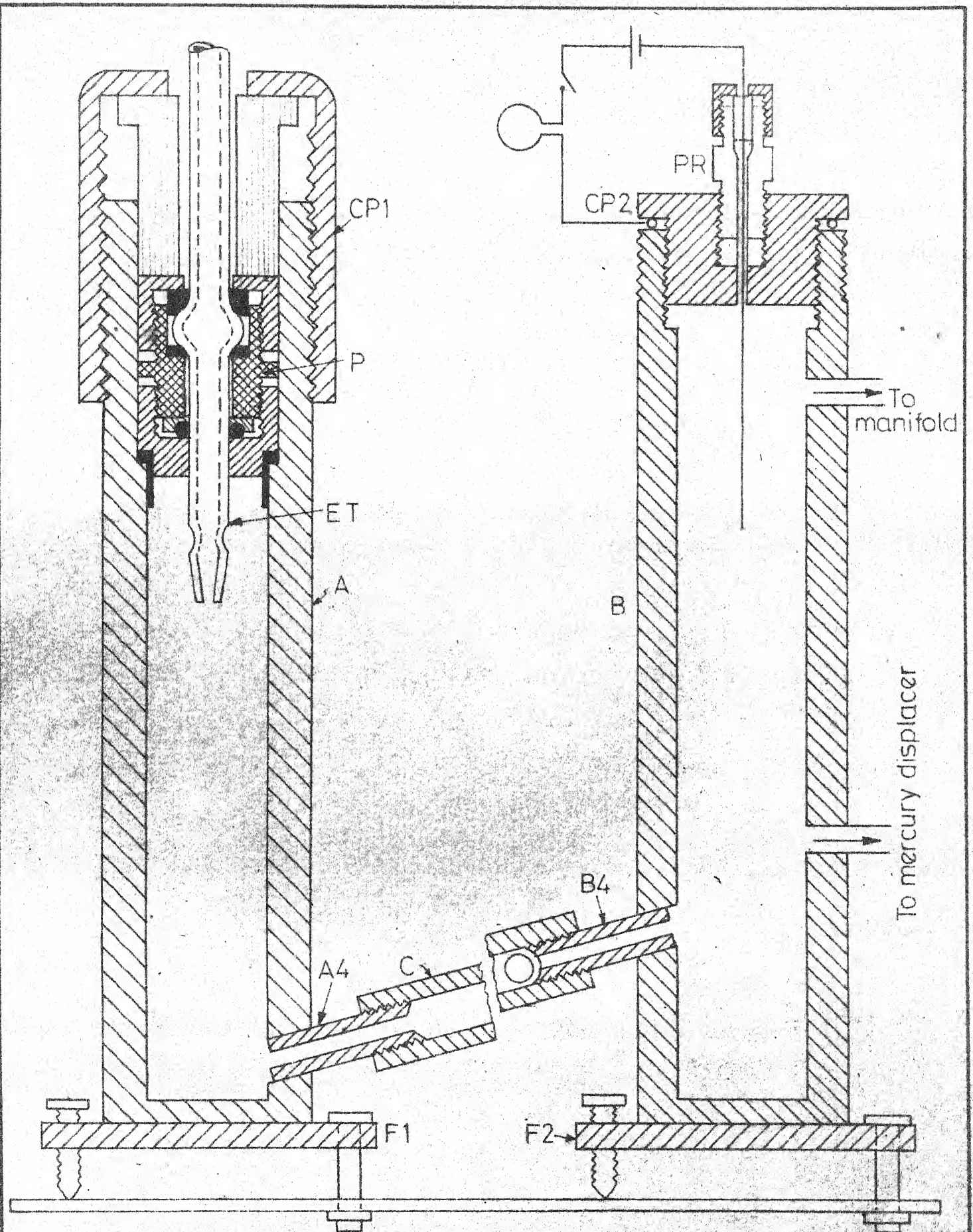


Fig. 4 - Compressor block assembly.

experimental tube should break under high pressure the sudden rushing of mercury from cylinder (B) to (A) will push the ball to the left extreme of C and closes the way between check valve (C) and cylinder (A), thus preventing the flow of mercury.

The cylinder (B) has two side lines. The lower line goes to a mercury storage unit called Mercury Displacer (MD) and the upper line goes to a manifold (MF) through which mercury in the cylinder (B) can be subjected to any pressure from high pressure nitrogen cylinder (N1). The cylinder (B) has a cap (CP2) which carries an electrical probe for indication of the maintenance of mercury inside B at the desired level. Since the heights of the experimental tube occupied by the sample are measured by means of a cathetometer for knowing the volume of sample, it is necessary to set the experimental tube vertical. This can be done by means of the leveling screws provided with the base flanges (F1) and (F2) of the two cylinder (A) and (B) of the compressor block.

Mercury Displacer: This is a cylindrical mercury storage and supply tank fixed horizontal to the working table. It has a threaded portion inside through which runs a piston. The lower side line of the cylinder (B) of the compressor block is connected to this unit. In order to facilitate correction for the mercury head in experimental tube to the

pressure of nitrogen gas in the manifold (MF) for calculation of exact pressure on the sample, it is necessary to maintain the mercury inside the cylinder (B) of the compressor block at a constant level. Any change in pressure of the sample at a constant temperature is associated with a change in volume of the sample gas which in turn results in a change in the level of mercury in the cylinder (B). Mercury displacer facilitates to maintain the mercury level in the cylinder (B) of the compressor block at a fixed height, as indicated by the probe (PR) by withdrawing or introducing some mercury from or to the compressor block. By rotating the piston forward, mercury is introduced into the compressor block (in case of compression of sample gas) and by rotating backward, mercury is withdrawn from the compressor block (in case of expansion of gas). The capacity of the displacer is 40 cc and hence can affect a maximum change of 40 cc of the sample.

Manifold: This is a hexagonal shaped metallic block having six outlets. It provides regulation of the pressure exerted on the mercury in the cylinder (B) of the compressor block by having access to the cylinder (B), the high pressure nitrogen cylinder (N1) and atmosphere via the valves (V1), (V5) and (V3). By properly operating these valves very small changes in the system pressure can be affected. MF connects an accumulation (AC) to the system via a valve (V2).

A1, when connected to the system, increases the volume of nitrogen gas in the set-up and thereby dampens small fluctuations in the nitrogen pressure in the set-up. An ordinary pressure gauge (PG) is used for the rough indication of nitrogen pressure in the system and a precalibrated precision bourdan gauge (PB) for the exact measurement of nitrogen pressure in the system. They are also connected to the manifold via valves (V4) and (V6) respectively.

(b) Vacuum System:

This is essentially to maintain a constant temperature around the experimental tube. The principle involved in this is that when a pure substance is boiled at a constant total pressure in an inert atmosphere the temperature remains constant. The principal part of this system is a double walled vapour jacket (VJ) surrounding the experimental tube (ET), the details of which are given separately in Figure 5, in which pure substance is boiled at a constant total pressure. The pure substance to be boiled is taken into the side arm boiling flask (BF) towards the bottom of VJ. The annular space between the two concentric tubes of VJ is silver lined leaving two diametrically opposite viewing slits. It is then evacuated and sealed under high vacuum. The viewing slits are provided so as to focus the cathetometer to the experimental tube inside VJ for measuring the height which the sample gas occupies. This silvering and evacuation of the annular space nearly eliminates heat losses

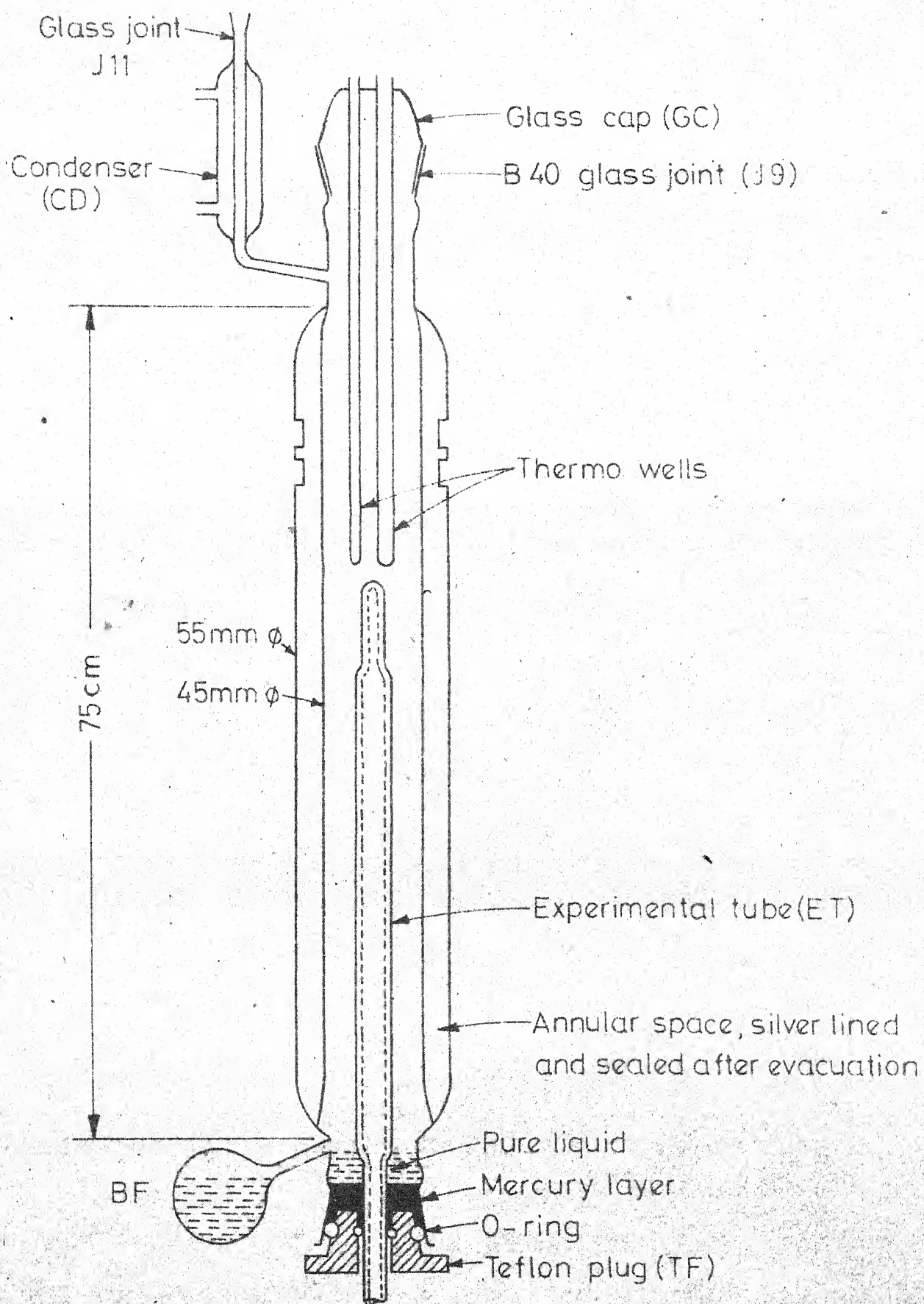


Fig. 5 - Vapour jacket.

from the vapour jacket (VJ) due to radiation and convection. VJ has a B40 glass joint (J9) at its top and a glass cap (GC) carrying two thermowells which protrude into VJ so that they are about 1" above the experimental tube (ET). Thermocouple is inserted into the smaller thermowell for temperature measurement. Bottom of VJ is closed with a teflon plug (TF) having a hole at its centre through which passes the experimental tube. O-rings are provided outside the teflon plug (TF) as well as inside the hole in order to make the bottom leak proof. A little amount of mercury is also poured on to the plug to form a mercury sealing over the plug as well as not to allow the liquid used in VJ to come in contact with O-rings.

The pure liquid to be boiled in the vapour jacket is charged into the side arm boiling flask (BF) and heated by means of a heating mantle around the flask. Power to the heating mantle is supplied from 220V mains through a variac. The vapour from the boiling flask rises in VJ and condensed vapour from the condenser (CD) at the top of VJ is returned to BF along the wall, thus forming a constant temperature vapour bath around the experimental tube (ET). The falling liquid from the condenser comes in contact with the rising vapour, thus maintaining the saturation temperature at the prevailing pressure. This ensures a constant temperature all along the length of VJ.

Nitrogen atmosphere is maintained in the glass manifold (M4) which is connected via an ice trap (T3) with glass joint (J10) to the top of the condenser (CD) of vapour jacket (VJ) by means of a vacuum hose and a B12 glass joint (J11). The ice trap (T3) condenses any vapour, possibly escaping from the condenser (CD), and thus prevents them to enter the manifold (M4). A mercury manometer (M5) is connected to the extreme left of the manifold (M4) for indication of nitrogen pressure in the system. The single arm side of a 3-way oblique-bored stop cock (S13) is connected to the manifold through the bulb (BP) and a 2-way stop cock (S14). One of the parallel arms of (S13) is connected to a nitrogen cylinder (N2), with a low pressure regulator by means of a thick rubber tubing. The other parallel arm is connected to a vacuum pump (MP), through an ice trap (T4) with glass joint J12 (not shown in Figure 1) by means of vacuum hoses. A stop cock (S16) is provided in this line with one way open to atmosphere for venting the pump when it is shut off after operation. The stop cocks (S13) and (S14) with the bulb (BP) can bring about small changes in the pressure of system, and hence small changes in the temperature inside the vapour jacket (VJ).

Two twenty liter flasks (BL1) and (BL2) are connected to the manifold (M4) via the stop cock (S15) by means of a thick walled vacuum hose. These flasks increase the volume

of nitrogen gas in the system and thereby dampen any fluctuations in the pressure in the system. The flasks are kept in a wooden box packed with insulating material so that any change in the ambient temperature does not cause any fluctuation in the pressure.

PROCEDURE:

This involves three steps: (i) Degassing of the sample; (ii) Loading of the degassed sample in the experimental tube and transferring the loaded tube from vacuum Loading Train to P-V-T apparatus, and (iii) Measurement of the P-V-T data.

(i) Degassing of the Sample: This done in the Vacuum Loading Train. Experimental tube is thoroughly cleaned with sulfuric acid + chromic acid mixture followed by repeated washing with distilled water. Later it is rinsed with acetone and finally dried in an oven for about an hour. A small steel ball which is also thoroughly cleaned and dried is inserted into the tube. Then the tube is fixed to the adaptor (AD) of vacuum Loading Train after inserting the packing gland (P) except for spacer on to the experimental tube. All stopcocks and joints except for those provided with mercury cups are greased with high vacuum grease Apiezon "N". About 50 cc of freshly prepared triple distilled mercury, enough to fill the whole of

experimental tube, is charged into the side arm flask (F6) of the unit (C1). The McLeod gauge flask (F7) is also charged with about 220 cc of mercury.

About 20 cc of sample to be degassed is taken into the removable flask (F5) and fixed in the vacuum loading train. Mercury is poured into the mercury cups around joints that cannot be greased. All the stop cocks except S5 are opened and the system is purged of air, through diffusion pump by the mechanical pump (MP) to its full capacity. The diffusion pump is never started until the system is evacuated to the full capacity of the mechanical pump alone. (About 1 mm. of Hg). While using the mechanical pump caution is taken in checking the ice trap (T2) from time to time and replacing water with fresh ice cubes. This evacuation of the system by mechanical pump is done as follows.

The stopcock (S11) is operated carefully to connect the system to the mechanical pump (MP) through the diffusion pump. The mechanical pump is put on after closing the stop cock (S12) and the system is evacuated so that the rise of mercury in the McLeod gauge is very slow. Evacuation is continued until the mercury level in the McLeod gauge just reaches the beginning of tube (C7). Stop cock (S11) is then cut off and turned to its other limb. Now the space over mercury in flask (F7) is evacuated slowly by carefully operating the stop cock (S10) to the system pressure which

is indicated by the just collection of mercury in the Mc-Leod gauge, back to the flask (F7). The above process, that is, first evacuating the system and then evacuating the space over mercury in flask (F7) is continued till the system is evacuated to the full capacity of the mechanical pump (MP).

The stop cock (S5) is momentarily opened to remove the air rich vapour over the liquid sample in flask (F5). The liquid sample is then frozen by keeping a Dewar flask containing dry ice + acetone mixture around the flask (F5). Now the stopcock (S5) is opened to the system and the space over the frozen sample in F5 is also evacuated by means of the mechanical pump alone for about an hour. During this period the sample should be in frozen state and ice should be present around the trap (T2). Then the stop cock (S5) is closed and diffusion pump (DP) is started as follows.

Circulation of cooling water (tap water) in the diffusion pump is started first. Liquid nitrogen is poured into the Dewar flask around the trap (T1). Power to the heating wire in diffusion pump is slowly given through the variac, say in steps of 10V, until the maximum allowable voltage, determined by the current rating and length of heating wire (in the present case 60V), is reached. The rate of condensation of mercury vapours should be between six to ten drops per

minute. The diffusion pump is always operated in conjunction with the mechanical pump and liquid nitrogen should be present always around the trap (T1) when diffusion pump is on.

From time to time vacuum attained in the system is checked by means of the McLeod gauge as follows.

The space over the mercury in the flask (F7) is slowly pressurised by connecting it to atmosphere by means of the stopcock (S10). The rise of mercury levels in the capillary (C4) and the comparison capillary (C5) should be slow and carefully observed. If the rising levels of mercury in the two capillaries are same, finally leaving no gap (observable by eye i.e. < 0.1 mm) inside the closed end of capillary (C4) the vacuum in the system is of the order of 10^{-6} mm of Hg (stick vacuum). After checking the vacuum in the system as above, mercury is slowly collected back into the flask (F7) by evacuating the space over mercury in this flask.

The stick vacuum is obtained in the system within an hour of starting the diffusion pump if the condensation rate of mercury in DP is maintained above six drops per minute. Initially the diffusion pump is usually run for about three to four hours to ensure the completion of degassing of the glass system.

Now the system is ready for degassing of the sample. Before each transfer, the space over the frozen sample is

pumped off by the diffusion pump for about 15 minutes. The flask containing the frozen sample is then disconnected from the manifold to evacuate the entire system excepting the sample to the stick vacuum. The diffusion pump is disconnected from the system, while transferring the substance, the reservoir containing the sample is brought to room temperature and the empty reservoir is inserted in the Dewar flask containing dry ice mixture and the stop cocks of these two reservoirs are opened. During this process all other stop cocks are closed. The sample slowly melts in (F5) and gradually gets collected in the flask (F4) because of the large temperature difference between the flasks (F5) and (F4). During this transfer the air and any other non condensable gases in the sample are released in the manifold (M1). This transfer is continued until a small residual amount of 0.1 cc is left in F5 and the stop cock (S4) of the reservoir containing the transferred sample is closed. Stop cock (S9) is now opened and the residue left in F5 is rejected to the liquid nitrogen trap (T1) and the system is pumped off to the stick vacuum by the diffusion pump (DP).

The process of distillation and pumping off the space over the frozen sample is repeated six to eight times. Initial transfer takes more time due to the presence of air and other non condensables in the sample. As the sample becomes devoid of these impurities, final transfer time will

be greatly reduced. After the final transfer the sample is stored in the flask (F4) and is kept in frozen state all the time until the loaded experimental tube is detached from the vacuum loading train.

(ii) Loading of the Experimental tube in the Vacuum Loading Train and Transfer of the Tube to P-V-T apparatus: All the stop cocks except the one containing frozen sample are opened and the system is pumped off by the diffusion pump for about two hours. During this process the manifold (M1) along with the precision tube (PC) and the experimental tube are gently heated up by winding a heating tape around them to degas the glass the system (to remove any substance adsorbed on the surface of the glass system during distillation).

All the stop cocks except S4 containing the sample and S6 are closed and Dewar flask containing dry ice + acetone mixture around the flask (F4) is kept around the tip of precision tube (PB) and a small amount of sample (say 0.1 cc) is collected in it. Then all the stop cocks except (S9) are closed and the system is evacuated to the stick vacuum. The liquid sample in PB is maintained at 0 °C and is allowed to reach equilibrium with its vapour at the room temperature in PC. Equilibrium is ensured by the constancy of the level of liquid in PC. Then the height in which the liquid sample

in equilibrium with its vapour, is confined in PC is measured by means of the Gaertner Cathetometer. From the calibration chart of PC the volume of the liquid sample in PC at 0°C and volume of its vapour at room temperature are obtained. Using the density of liquid at 0°C and ideal gas law for its vapour at room temperature the total number of moles in PC are calculated. By carefully keeping the liquid nitrogen flask around the tip of the experimental tube and opening the stop cock (S8) only, all of the sample in PC is collected at the tip of the experimental tube. This sample is always kept in frozen state until the tube is transferred to the P-V-T apparatus. After the complete transfer of the sample in PC is ensured. Stop cock (S9) and (S7) are opened while running the diffusion pump. The side arm flask (F6) of the unit (C1) is slowly tilted to see that mercury trickles down along the tube (C2) slowly and drop wise fills up the experimental tube. Mercury-drops, as they leave the nozzle of the tube (C3), expand and any entrapped air in the mercury is rejected to the trap (T1) because of the diffusion pump (DP). The experimental tube is thus filled up with the air free mercury completely. All the stop cocks are then closed.

The experimental tube containing the frozen sample, now sealed with mercury, is removed from the vacuum loading train after bringing the unit (C1) and adaptor (AD) to

atmospheric pressure by removing the mercury in the mercury cups around the joints (J2) and (J4). As soon as the tube is removed from the vacuum loading train along with liquid nitrogen flask around its tip, the tube is closed by the fore finger finally leaving no gap at the top. It is then brought to the compressor block of P-V-T apparatus which is filled up with pure freshly distilled mercury. The mercury in the cylinder (B) of compressor block is subjected to small pressure from the nitrogen cylinder (N1) to bring the mercury level in cylinder (A) to its surface. The experimental tube while closing with the fore finger, is removed from liquid nitrogen flask, and carefully inverted, into the mercury of the cylinder (A) of the compressor block. The fore finger is then carefully removed seeing that no air enters the tube. The tube with the packing gland (P) is then slowly pushed on to the seat inside the cylinder (A) while slowly releasing the nitrogen pressure on the mercury of cylinder (B) so that no air gap is left between the packing gland (P) and the mercury inside the cylinder (A). Then the spacer of the packing gland is inserted on to the experimental tube and the cap QP1 is firmly tightened to the cylinder (A) pushing the whole packing gland (P) on to the seat inside the cylinder (A).

(iii) Measurement of P-V-T Data:

A few adjustments are made before actual measurements. Care is always taken in seeing that the sample never expands enough to enter into the compressor block. The sample is usually either kept under pressure or an ice-water bath is kept around the sample while adjustments are made.

The piston (D3) of the mercury displacer is rotated forward and all the mercury in the displacer is displaced into the compressor block. The cap CP2 of the cylinder (B) of the compressor block is opened carefully. The mercury inside the cylinder (B) is then adjusted to the desired level, in between the two side tubes of B, by either adding or removing some mercury to or from the cylinder (B). The length of the tungsten wire is then adjusted to the level of mercury inside B and is accurately measured by means of a cathetometer before fixing the cap CP2 to the cylinder (B). The experimental tube is then adjusted vertical by means of the leveling screws of the base flanges F1 and F2 of the compressor block with the help of a plumb-bob and the compressor block is fixed firmly to the working table.

The teflon plug (TF) of the vapour jacket (VJ) is slipped on to the experimental tube with O-rings inside the hole and outside the plug. VJ is then clamped around the experimental tube and the plug (TF) is carefully tightened to the bottom of VJ. Pumice stones are inserted in the boiling flask (BF) of the vapour jacket (VJ) before fixing

it around the experimental tube. Mercury is poured on to the plug (TF) to height of one centimeter by means of a long glass funnel. Bromo-benzene vapour serves best as the heating medium for the present investigation. About 150 cc of pure Bromobenzene is slowly poured over the mercury so that it over flows into the side arm boiling flask (BF). The glass cap (GC) is then inserted on the top of the vapour jacket. High temperature cum high vacuum grease Apiezone-T is used to grease the joint J9. The condenser (CD) of the vapour jacket is connected to the trap (T3) of the manifold (M4) by means of a flexible vacuum hose and B12 glass joint (J11). Silicone oil is poured into the thermowell of the vapour jacket in which the hot junction of the thermocouple is inserted.

The vacuum system, including the balasts BL1 and BL2 and the vapour jacket (VJ), is evacuated and flushed with nitrogen gas from the cylinder (N2) several times to remove air in the system. The system is then filled with nitrogen gas to the vapour pressure of bromobenzene corresponding to the temperature at which the sample is to be maintained. Power is supplied to the heating mantle for heating the boiling flask (BF). Circulation of the tap water is started in the condenser (CD). The reference junction of the thermocouple is maintained at 0°C by replacing the melted water from time to time by fresh ice cubes in the flask around the cold junction.

Temperature inside VJ is noted frequently by means of a precalibrated thermocouple. The details of calibration are given in Appendix B. When the temperature attains a steady value, nitrogen pressure in the manifold (MF) of the pressure system is varied over a range in small decrements from a high pressure (when the sample is in liquid state) to a low pressure until the sample is expanded to the maximum permissible volume limited by the experimental tube capacity. The sample is agitated by moving the steel ball by means of a permanent magnet. For each pressure the level of mercury inside B of the compressor block is adjusted to the tip of the tungsten wire of the probe (PR) by withdrawing mercury to the displacer (MD). After the attainment of equilibrium is ensured, the height of the sample as well as the heights of mercury and liquid meniscie are measured accurately by means of the cathetometer. Equilibrium is ensured by the constancy of the volume of the sample over a period of time when the temperature and pressure are maintained constant. The volume readings are taken in the 3 regions namely:

- (i) Liquid state
- (ii) Liquid-plus vapour state and
- (iii) Vapour state

The volumes are determined from the heights measured and the calibration chart of the experimental tube. After the full range of volume is covered for an isotherm, the temperature of

the sample is changed by changing the nitrogen pressure in the vacuum system. The above procedure is repeated for the desired range of temperature.

CHAPTER III

FABRICATION DETAILS

COMPRESSOR BLOCK:

This unit consists of two hollow upright cylinders A and B with a check valve assembly C' connecting the two cylinders. The fully assembled compressor block is shown in Figure 4. Mercury in the compressor block provides a continuous path from high pressure nitrogen gas over mercury in upper portion of cylinder B to the sample confined in the top portion of experimental tube, which is held firmly and vertically from the cylinder A. Since the compressor block contains mercury inside it was first intended to use stainless steel as the material of construction. But due to unavailability of the material to suit the requirements and high costs involved, an alternative method was adopted. A composite pressure-fit assembly was made with an internal stainless steel pipe, fitted into a Nickel chrome pipe, to construct cylinders A and 'B'. The detailed drawings with the dimensions of these parts are given in Figures 6, 7, and 8.

A thick walled stainless steel pipe (A1) of 1" I.D. and a Nickel chrome pipe (A2) were machined to the dimensions as given in Figure 6. A step of 3 1/4" depth was cut from one end of A1* on which rests the experimental

tube with the packing gland. The other end of A1 was closed by push fitting a $1/4$ " thick stainless steel disc.

One end of A2 was threaded outside for a length of $2\frac{1}{2}$ " on to which fits a cap (CP1). The other end was closed by welding high quality M.S. rod (A3) of $1\frac{1}{2}$ " length, after push fitting A1 inside A2. A3 was threaded for a length of $7/16$ " for fixing the base flange (F1) to the cylinder A. After assembling the parts A1, A2 and A3, a hole of $1/4$ " diameter was drilled about 1" from the bottom at an angle of 30° upwards from the horizontal. This hole was then internally threaded by running a tap. A side limb (A4), the dimensions of which are given in Figure 8, was screwed inside and permanently welded.

Similarly the cylinder 'B' was made by push fitting a stainless steel pipe (B1), closed at one end by welding a stainless steel disc, in a Nickel chrome pipe (B2) and welding a high quality M.S. rod (B3) at the bottom. The dimensions of (B1), (B2) and (B3) are given in Figure 7. Then a hole, inclined downwards at an angle of 30° from the horizontal, was drilled at a height of $2\frac{1}{4}$ " from the bottom. This hole was internally threaded by running a tap inside so as to screw the side limb B4, the dimensions of which are given in Figure 8, and weld it. Two more holes were drilled on the cylinder 'B' at distances of $3\frac{1}{2}$ " and 8" from the open end of B into which two $1/4$ " O.D.

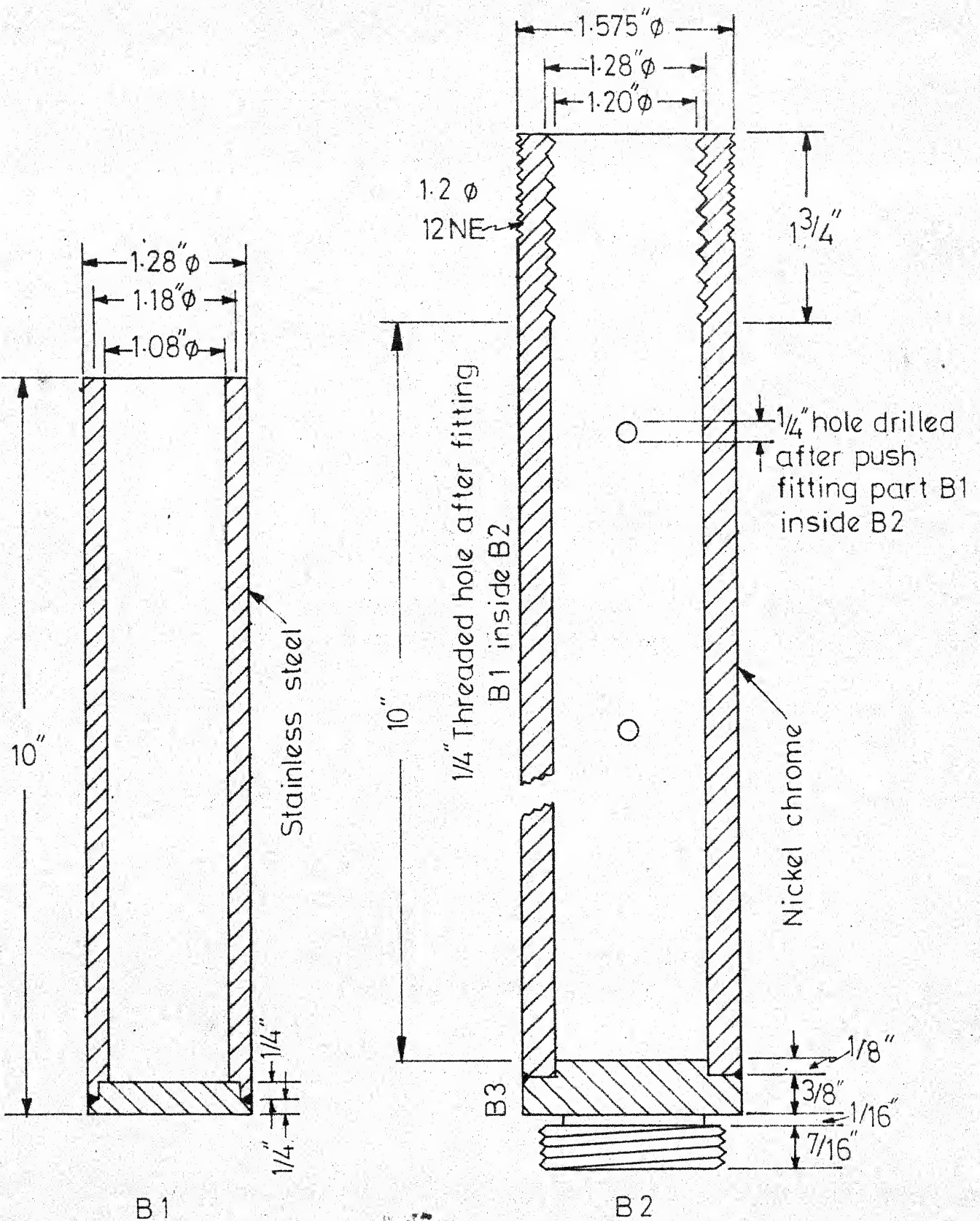


Fig. 7 - Cylinder (B) of compressor block.

thick walled stainless steel tubes, having A.E cone fittings at one end, were welded. The upper stainless steel tubing connects the top of the compressor block to the manifold (MF) through which nitrogen pressure was exerted on the mercury in the cylinder B. The lower tubing connects the lower part of cylinder B. The mercury level in cylinder B was maintained constant in between these two side tubings.

The side limbs (A4) and (B4) were made out of high carbon steel rods and along with a piece C, the dimensions of which are given in Figure 8, they form a check valve assembly as shown in Figure 4. A4 and B4 had ~~had~~ through holes of $1/8$ " diameter and tapered seats at the open ends. A4 had left hand threads externally for about $1/2$ " length at open end. Similarly B4 had right hand threads externally for the same length. C had a through hole of $1/4$ " diameter and accordingly had its ends threaded internally so as to fit into the side limbs A4 and B4. Teflon tape was used to ensure these threaded joints leak proof. A small steel ball of diameter $3/16$ " was inserted in C before fixing it to the side limbs A4 and B4 so that it can move freely in C but cannot pass through the limbs (A4) and (B4).

The details of the base flanges (F1) and (F2) which are indential are given in Figure 8. They were made out of high carbon steel and had six holes of $1/4$ " diameter

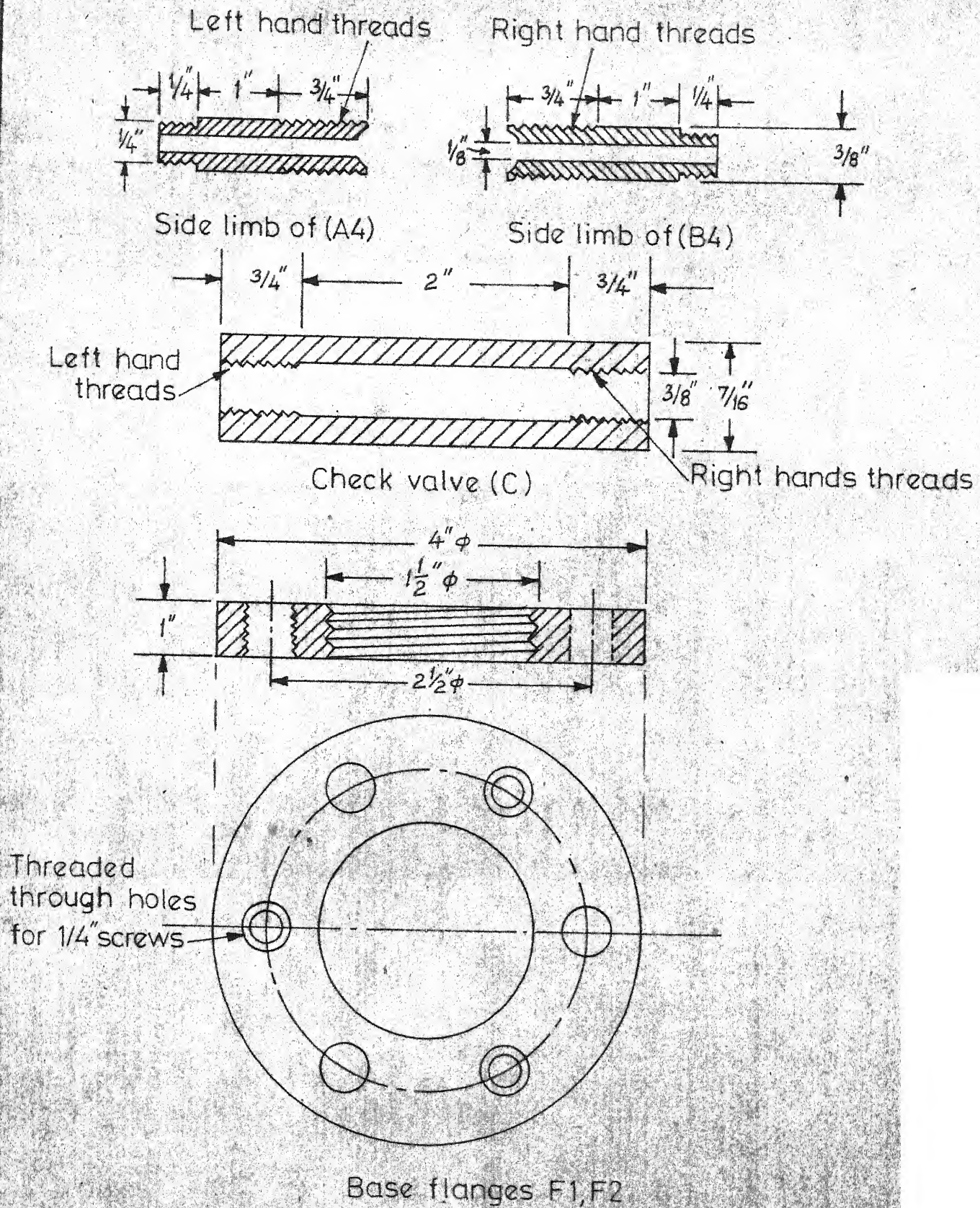


Fig. 8 - Other parts of compressor block.

at a radius of $1\frac{1}{4}$ ". Three of these holes were threaded for the leveling screws. The other three holes were used for fixing the compressor block as a whole on to the working table. The experimental tube, held from the cylinder A of compressor block, can be adjusted vertical with the help of the leveling screws.

The details of the caps (CP1) and (CP2) of cylinders A and B are given in Figure 9. Both of them were made out of high carbon steel. The cap (CP1) had a hole of $\frac{5}{8}$ " diameter, through which passes the experimental tube. CP1 when tightened, pushes the packing gland firmly against the step inside the cylinder A and prevents leak along the wall of A through the step, forming access to the packing gland. The cap (CP2) of the cylinder B was threaded externally to fit into the cylinder B. It was also provided with an O-ring groove on the seat which sits on the edge of cylinder B to prevent the leakage of nitrogen gas along the threads. CP2 had a threaded axial hole of $\frac{3}{4}$ " diameter to a depth of 1" from the top to fix the probe (PR). Teflon tape was used to ensure the threads leak proof. CP2 also had a through hole of $\frac{1}{8}$ " diameter through which the level sensing element (Tungsten wire) of the probe (PR) passes into the cylinder B. (PR) was a 'CONAX' buffalo (N.Y.) type (imported) probe which ensured that mercury inside the cylinder B was maintained at the desired level. PR had a

teflon piece inside, having a hole of 0.1 mm diameter through which the tungsten wire (level sensing element) passes into the cylinder B'. Above the teflon piece there was a pusher with lock which compresses the teflon piece as the head of the probe was tightened, gripping the wire firmly and hence resulting in a leak proof joint. The length of the tungsten wire inside the cylinder B was adjusted to the level at which the mercury inside B was to be maintained and accurately measured before fixing the cap (CP2) to the cylinder B. It was ensured that the wire does not touch any metallic parts of the cap (CP2) and cylinder B' inside. The wire was externally connected to the cylinder B through a cell, an electric bulb, and a switch. Lightening of the bulb indicated the maintenance of mercury at the desired level inside B.

PACKING GLAND:

This was designed for providing a pressure tight fitting between the metallic cylinder A of the compressor block and the glass experimental tube (ET).

The original design of Kay and Mamata Dutta⁸, was tried first. It did not turn out to be successful because of the non-availability of the soft rubber, that could be machined accurately, sealing the experimental tube as in the design. Also, the very small width of the step inside the cylinder A did not allow use of any O-ring to prevent

leak along the wall of cylinder A through this step. As a result, even mercury was leaking through the seat as well as along the surface of the experimental tube. So it was found imperative to provide a new design.

The details of this design are given in the Figure 9.

A teflon washer (P1) was provided on the step of cylinder A to prevent any leak between the walls of "A" and the packing gland as a whole through the step. To prevent the leak along the surface of experimental tube an O-ring (P3) was provided on the seat inside the house (P2). P2 was internally threaded. A driver (P5) was fitted into P2. To compress the O-ring uniformly against the surface of the experimental tube a pusher (P4) was provided over the O-ring (P3) between the seat of house (P2) and the driver (P5). As the driver was tightened inside P2, the pusher (P4) pushes the O-ring against the surface of experimental tube and thus prevents the leak along the surface of the experimental tube. The driver (P5) had a hole of $5/8$ " diameter to a depth of $5/8$ " in which the bulb of experimental tube rests. To prevent the bulb from directly coming into contact with the metal, a rubber washer was provided here. A cap (P6) was screwed over the bulb to the threaded portion of the driver at the top to hold the bulb (and so the experimental tube) intact, while pressure was exerted on the sample inside the experimental tube. Also another rubber washer was provided between

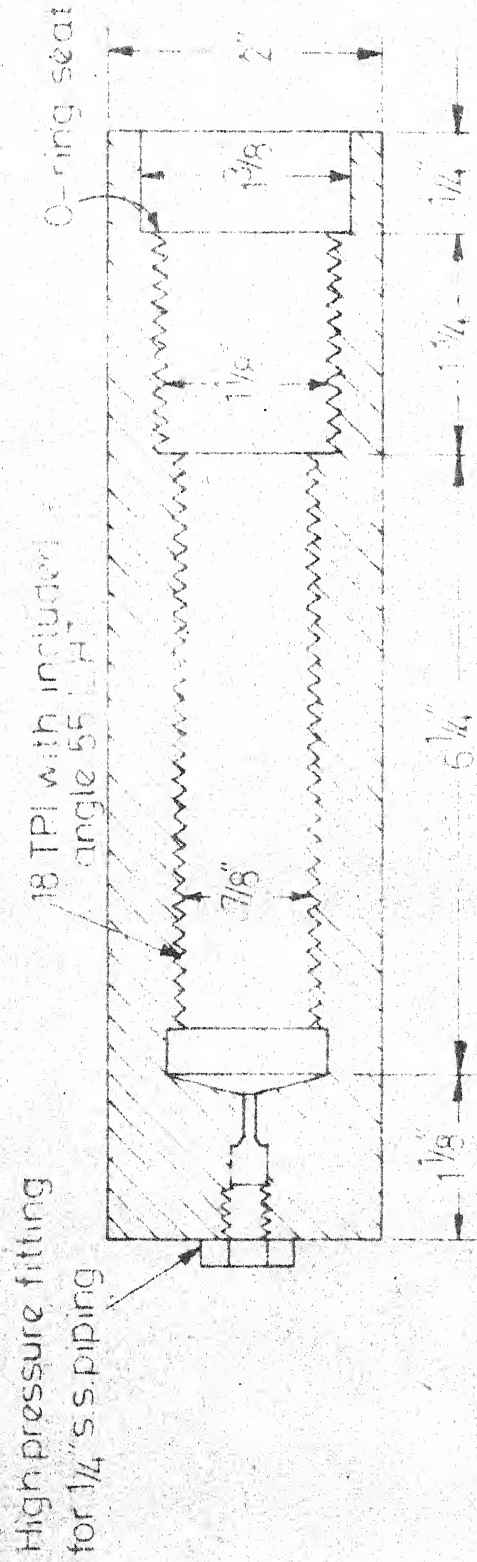
the top of the bulb and the inside surface of the cap (P6) to prevent glass bulb from directly coming into contact with the metallic cap (P6). A spacer (P7) over the cap (P6) pushes the whole of packing gland against the step compressing the teflon piece (P1) as the cap CP1 of the cylinder 'A' was tightened.

MERCURY DISPLACER:

This is essentially a mercury storage and supply tank. Changes in volume of the sample in the experimental tube were affected by displacing mercury in or out of the compressor from this unit, Without changing the mercury level in the cylinder 'B' of the compressor block. It was designed for displacement of a maximum of 40 cc of mercury. Accordingly a maximum of 40 cc could be changed in the volume of the sample.

It consists of five component parts: a mercury storage space (D1), a piston (D3), a piston supporter (D2), teflon packing (D4), and a packing pusher (D5). All the components were made out of high carbon steel and later electroplated with Nickel Chromium.

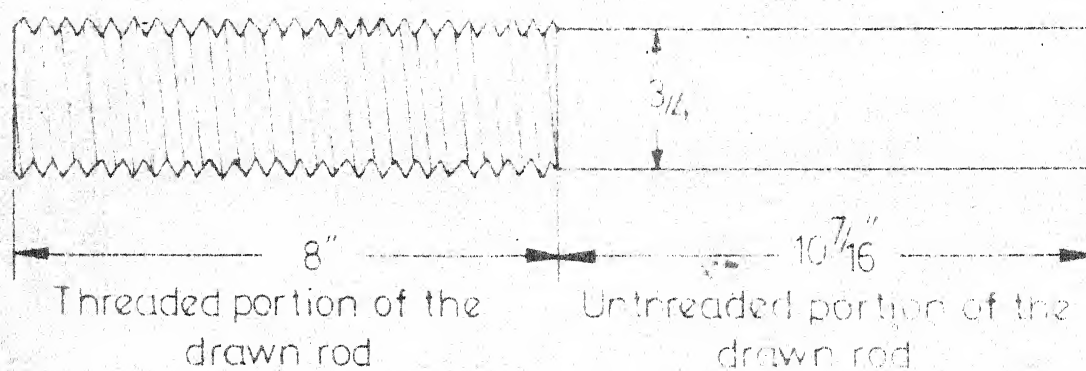
The detailed figures with dimensions of these components are shown in Figures 10 and 11. D1 and D2 were made out of 2" diameter rod. D1 contained female part of A.E. cone fitting at one end to take the connection from the cylinder 'B' of compressor block. The other end was



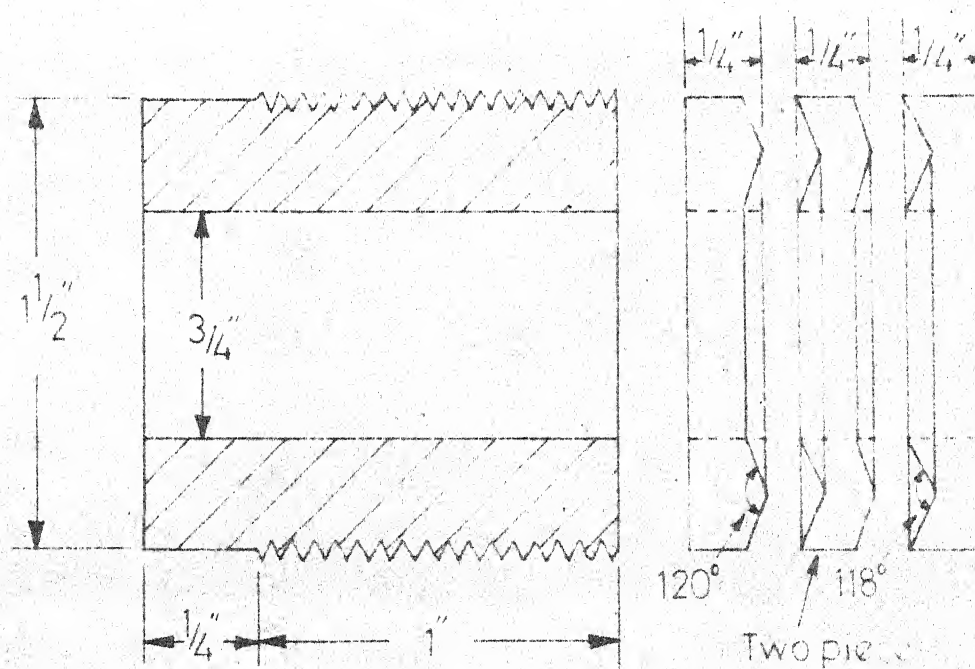
Right hand threads to suit the part D1



Fig 10 - Mercury displacer



PART D3 (Piston)



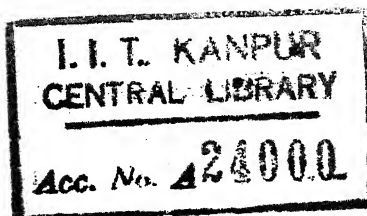
PART D5 (Pusher)

PART D4

This will go into right part (Teflon packing rings) of D2.

Fig.11 - Mercury displacer.

accordingly threaded for a length of $1\frac{3}{4}$ " with a provision for O-ring groove to take the part D2. The middle portion (about $6\frac{3}{4}$ ") had fine threads (18 TP1) in which the piston D3 runs. These threads were made fine in order to accomplish very small displacements of mercury resulting very slow but controlled rate of changes in volume of the sample. D2 was threaded at one end to fit into D1. It had through hole of $7/8$ " diameter in which the unthreaded portion of the piston D3 runs. At a depth of $2\frac{1}{2}$ " from the other end a step was cut inside D2 on which the teflon packing D4 rests. At this end it was internally threaded to screw the packing pusher D5. After fixing the piston D3 inside the body of the displacer, teflon packings (rings) were pushed on to the seat of D2 from its open end and D5 was tightened. As D5 was tightened the teflon rings expand laterally and firmly grip the unthreaded portion of the piston uniformly around its surface and prevents any leakage of mercury along the surface of the rod. This type of packing replaced the dynamic O-rings which should have been used but for their non-availability. The portion of the piston which runs inside the body of D1 was only threaded and the rest of its length was finely polished. This piston had a removable handle at its open end to facilitate its easy turning. The displacer was horizontally fixed on two wooden supports which were screwed to the working table.



MANIFOLD:

The manifold (MF) formed a junction interconnecting different parts of the pressure system and regulated the control of pressure in the system.

This was made out of a 1" thick hexagonal brass plate as is shown in Figure 12. It had six faces each having a drilled hole meeting at the centre thus forming a 6-way junction. All the six faces had female parts of high pressure fittings for connecting different parts with 1/4" O.D. thick walled stainless steel tubing. Auto clave Engineers cone type of fittings were used. The manifold had three 1/4" diameter threaded holes to a depth of 3/4", perpendicular to its face. These were used to fix the manifold to the pannel near the working table by means of 2" long 1/4" screws.

The upper side of tube from the cylinder 'A' of the compressor block was connected to the bottom face of MF through a Hokes globe valve (V1) (on-off type). V1 was used to facilitate the checking of leaks in the system and did not play any role in regulating the nitrogen pressure in the cylinder 'B'.

An empty oxygen cylinder (AO) having a capacity of 1.5 cu.ft. served as an accumulator to the system. This was connected to the manifold through a Hoke's globe valve (V2). The accumulator increases the volume of nitrogen gas

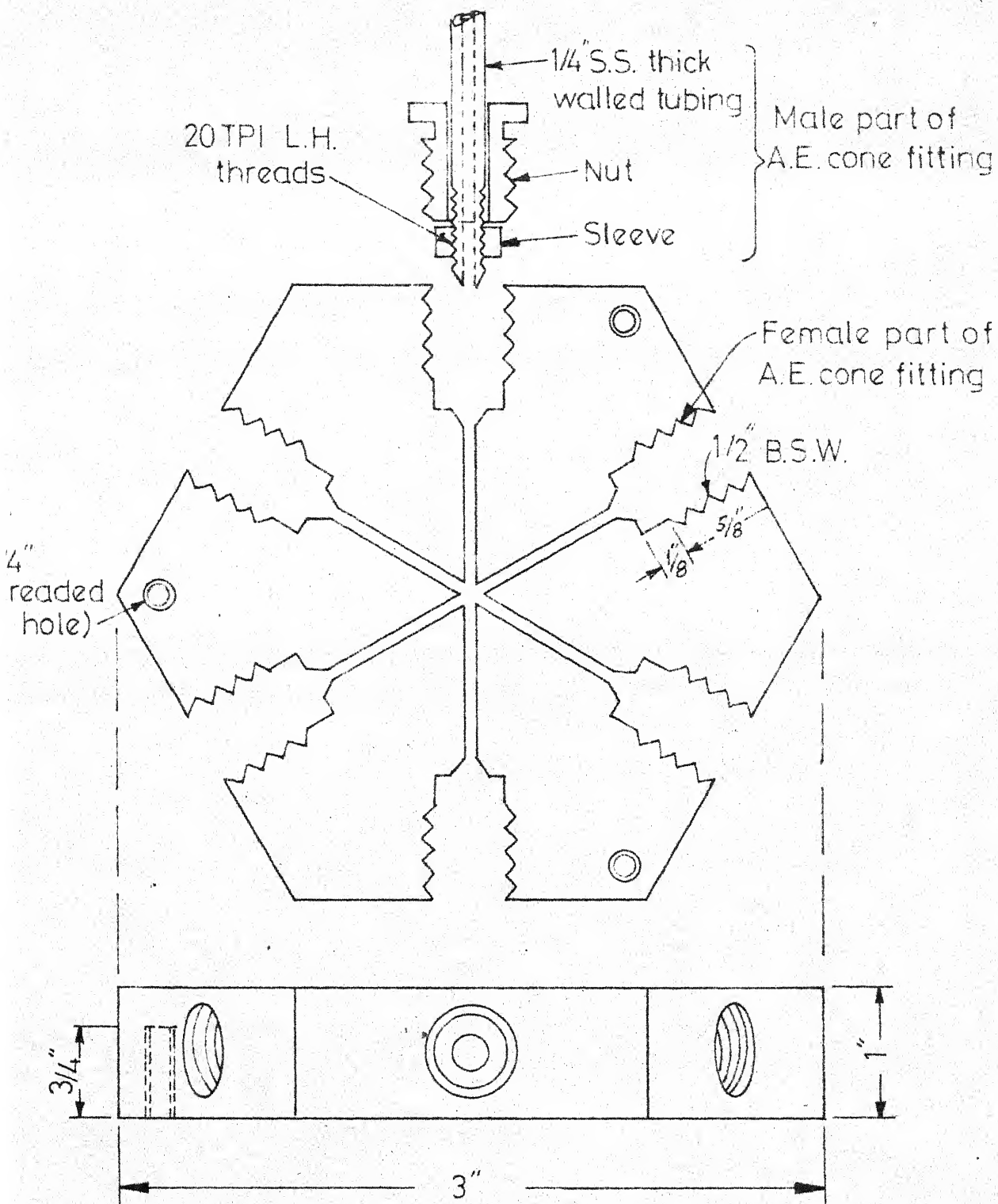


Fig. 12 - Manifold with fittings.

in the system and dampens any pressure fluctuations in the system.

A pressure gauge (PG) of 0-300 psia range ~~was~~ was attached to the manifold (MF) through a globe valve (V4) for rough indication of pressure in the system.

The manifold (MF) had access to the atmosphere through a needle valve V3 which provides slow but controlled reduction of pressure in the system by bleeding nitrogen off.

The mercury in the cylinder B of the compressor block was subjected to nitrogen from a high pressure nitrogen cylinder (N1) with regulator through the manifold. A needle valve (V5) similar to (V3) was provided between N1 and MF for fine regulation of gas from N1.

A precision bourdan gauge of 16" diameter (Seegers Instrument Co.) was connected to the remaining face of MF for the exact measurement of nitrogen pressure in the system. A needle valve (V6) similar to that of V5 and V4 was provided in this line so as to slowly bring this gauge to the system pressure. This gauge was checked for calibration against standard dead weight gauge. The details of the calibration are given in Appendix 'C'. For different ranges of pressure measurement different gauges were used, they being, for low pressure, 0-30 psia gauge with smallest division of 0.05 psi, for intermediate pressures, 0-300 psia ranged gauge and for high pressure, a 0-1000 psia ranged gauge.

CHAPTER IV

RESULTS, DISCUSSION AND CONCLUSIONS

Vapour pressures of monochlorobenzene were determined in order to standardize the performance of the entire set-up and to find its limitations. The pressure, volume, and temperature readings were taken after equilibrium was ensured by the constancy of the readings over a period of one hour. The vapour pressure of the sample was obtained after making a series of corrections to the nitrogen pressure at the interface in the cylinder (B) of the compressor block. The nitrogen pressure at the interface in the cylinder (B) was taken as the nitrogen pressure in the manifold (MF), and was read by a precision bourdan gauge (PB). The corrections applied were (i) the hydrostatic head of the mercury column in the experimental tube, (corrected to 0°C) above the interface of the mercury and the nitrogen gas in the cylinder (B) of the compressor block. This comprises two zones, namely (a) hot zone inside the vapour jacket and (b) cold zone outside the vapour jacket at the room temperature. Corrections were applied to these two zones separately. (ii) Hydrostatic head of the liquid sample between the sample vapour and the mercury column in the experimental tube. (iii) Partial pressure of mercury in the sample vapour which was taken as the vapour pressure of the mercury at the prevailing temperature. (iv) Pressure correction due to the capillary effect of the

sample tube.

With reference to Figure 13 , the vapour pressure of the sample is given by the following expression:

$$P_{\text{sample}} = P_N - P_{\text{HM}} - P_{\text{HL}} - P_{\text{VM}} - P_{\text{cap}}$$

where P_N = Nitrogen pressure in the manifold

P_{HM} = Hydrostatic head of the mercury

P_{HL} = Hydrostatic head of the liquid sample

P_{VM} = Vapour pressure of mercury

P_{cap} = Pressure correction due to capillary effect of the experimental tube.

The height of the closed tip of the experimental tube above the tip of the probe (PR) inside the cylinder (B) of the compressor block was measured five times by means of the cathetometer and the average value of the five observations was ≈ 77.6533 cm. Thus P_{HM} was obtained by the following expression:

$$P_{\text{HM}} = 77.6533 - \text{HMH} \left(\frac{\rho_{\text{HH}}}{\rho_{\text{HO}}} \right) - \text{HMC} \left(\frac{\rho_{\text{HC}}}{\rho_{\text{HO}}} \right)$$

where HMH = height of the mercury column in the experimental tube in the hot zone and

HMC = height of the mercury column above the tip of the probe upto the hot zone of the mercury column in the experimental tube. ρ_{HH} = density of the mercury in the hot zone. ρ_{HC} = density of the mercury in the cold zone. ρ_{HO} = density of the mercury at 0°C.

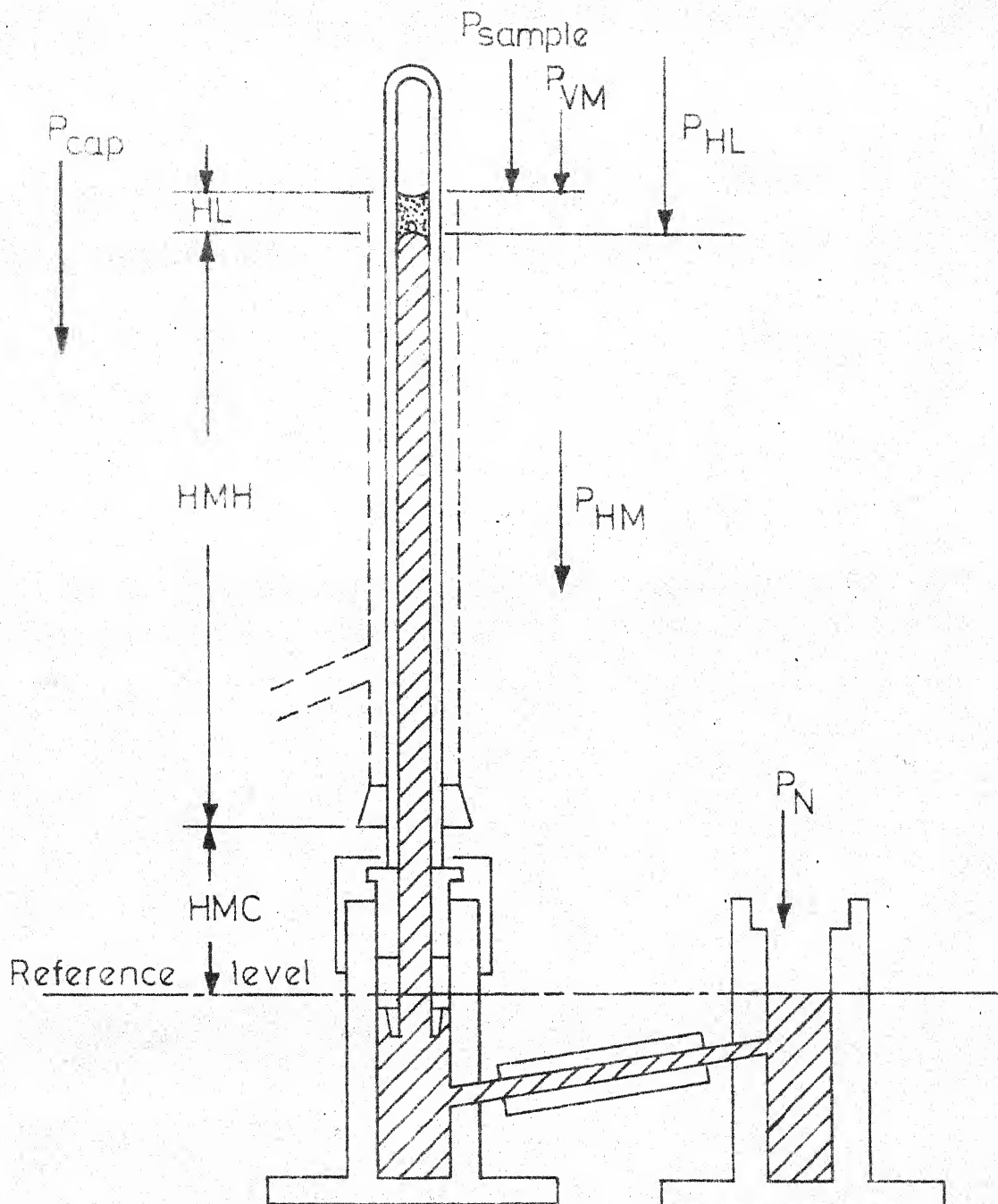


Fig.13 - Schematic diagram of Mercury Heads.

Pressure correction due to the hydrostatic head of the liquid sample is given by

$$P_{HL} = HL \frac{\rho_{LH}}{\rho_{HO}} \quad (\text{Density of liquid at the prevailing temperature})$$

where HL = height of the liquid sample layer on the mercury column in the experimental tube.

However, the variation of the densities of the liquid sample and mercury with temperature could not be found significant in the present analysis because of the presence of the traces of air in the sample. Also the correction for partial pressure of mercury was not taken into account as the vapor pressures of the mercury at the working range of temperatures is very low. The capillary correction was negligible as the minimum size of the inside bore of the experimental tube is 6 mm.

The vapour pressures obtained in the present work along with the reported literature values were shown in Table I. The data obtained shows high positive deviations. These deviations are attributed to insufficient degassing of the sample before loading. Also, the data were taken after a long time interval from degassing and loading of the sample, during which period the dissolved air in the mercury in the experimental tube and compressor block had diffused into the sample. The time gap could not be avoided as the mercury displacer, all on a sudden, started leaking after loading the sample and consumed considerable amount of time for

TABLE I

VAPOUR PRESSURE OF MONOCHLOROBENZENE

Sl. No.	Temperature	State	Volume	Pressure in present work	Literature value
1.	88.08	L+V	0.4655	232.3	197.8
		L+V	5.5471	228.9	197.8
		L+V	10.4855	223.7	197.8
2.	101.92	L+V	0.4725	349.6	315.5
		L+V	6.0965	332.2	315.5
		L+V	10.5551	328.4	315.5
		L+V	15.4591	323.2	315.5
3.	117.60	L+V	1.3324	561.2	511.3
		L+V	5.7480	531.9	511.3
		L+V	10.5982	520.1	511.3
4.	133.08	L+V	0.4085	849.5	789.4
		L+V	5.7536	840.5	789.4
		L+V	14.5615	804.1	789.4
5.	143.57	L	0.2445		
		L	0.2456		
		L	0.2465		
		L+V	0.2166	1309.3	1037.4
		L+V	7.172	1083.3	1037.4

repairing. The deviation of data due to presence of air in the sample was further confirmed by the fact that the deviations are smaller the larger are the volumes of the sample.

The virial coefficient data could not be taken because of the limitation of the maximum volume of the experimental tube and the sample loaded initially was too large to allow its complete vaporization.

It is concluded from this investigation that the sample loaded in the experimental tube should be highly pure. Degassing should be performed with the greatest possible efficacy and the data should be taken immediately after loading. The mercury should be freshly distilled and devoid of any air. The amount of sample loaded in the experimental tube should be predetermined so as to allow complete vaporization of the sample in the given volume of the experimental tube. For ease of operation, the effective volume of the experimental tube should be increased. This can be easily achieved by replacing the straight-bore experimental tube with a precalibrated tube comprised of several bulbs connected by small capillaries. Accordingly the volume of the mercury displacer also should suit the experimental tube. This can be achieved by adding an additional mercury reservoir under the manifold pressure from which mercury can be withdrawn to and from the displacer, as and when it is necessary. All brazing joints should be avoided as far as possible and

replaced by high pressure fittings. The agitation of the sample should be done more vigorously in order to reduce the time lag necessary for attainment of equilibrium. This can be achieved by replacing the permanent magnet with a more powerful electromagnet.

On incorporating the above mentioned simple modifications an all-proof set-up for measurement of the second virial coefficient will result.

APPENDIX A

CALIBRATION OF EXPERIMENTAL TUBE

Calibration of the experimental tube comprises establishing a relation for the volume of the experimental tube from the closed end to any plane perpendicular to the axis of the tube as a function of the distance from the outside edge of the closed tip.

Accurately weighed amounts of mercury were poured into the experimental tube at instalments and the corresponding heights occupied by the mercury were determined. Special care was taken in seeing that all of the weighed amount of mercury formed the column of mercury and no globules of mercury were lost in pouring. From the knowledge of the density of mercury at the temperature when the heights were measured the volumes of the experimental tube at various levels were obtained.

Heights were accurately measured by means of a Gaertner's precision cathetometer, which can read up to 0.0001 cm. The range of cathetometer is 10 cm. Since the experimental tube was to be calibrated for about 40 cm. length, this full length was divided into five parts each of length 8 cm. roughly and sharp reference marks were etched on the experimental tube.

Calibration was conducted in a room where temperature and humidity were fairly constant. The experimental tube was

thoroughly cleaned with sulphuric acid chromic acid mixture followed by repeated washing with distilled water. Later it was rinsed with acetone and finally dried in an oven for about an hour, before starting the calibration.

The experimental tube was held in the inverted position by means of a retort stand and was adjusted vertical from time to time with the help of a plumb bob. The cathetometer was placed at a distance of about 5 cm. from the tube. The height of the tube was adjusted in such a way that the closed tip fell in the range of 0 to 1 cm reading of the cathetometer. Pure air free mercury (about 10 to 15 grams), accurately weighed in a Metler balance, was slowly dropped into the tube by means of a long drawn glass funnel. Any air trapped between the wall of the tube and the mercury inside was removed by means of a finely drawn glass capillary so that when tube was focussed by the cathetometer a mirror like image of mercury was in view. The height of the mercury in which the weighed amount of mercury was confined and the height of the mercury meniscus were determined. Temperatures near the experimental tube before and after the measurement of heights were noted by means of a calibrated mercury-in glass thermometer. An incremental weighed amount of mercury was then added and the heights as well as the temperatures were determined as in the previous case. This procedure was repeated until the mercury column inside the tube reached the first reference

line etched on the tube. In all the cases outside edge of the closed tip was taken as the reference mark for measuring the heights.

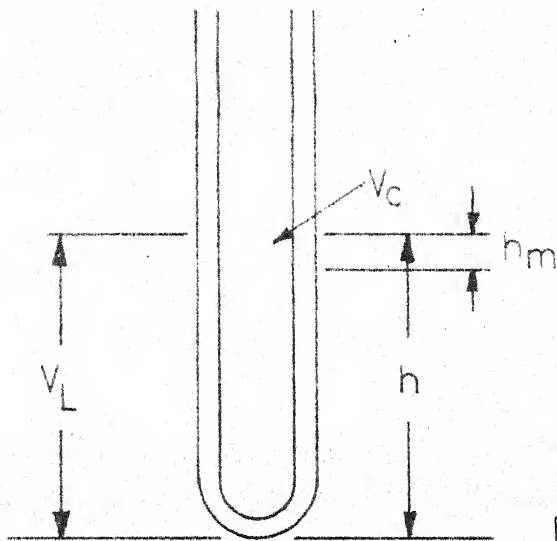
The experimental tube was lowered so that the first reference line fell within the range of 0 to 1 cm. reading of the cathetometer and the above procedure was continued until the mercury column inside the tube reached the second reference line etched on the tube. In these cases first reference mark was taken as the reference in measuring heights. Later, the distance between the outside edge of the closed tip and the first reference line was added to all heights to get the required heights from the closed tip.

The same procedure was continued for the entire length of the tube.

CALCULATIONS:

With reference to figure A, the level volume (V_L) is defined as the volume enclosed between the closed end and any plane perpendicular to the axis of the tube at a distance 'h' from the outside edge of the closed end of the tube.

The level volume for each calibration point was obtained by adding to the volume of mercury V_{Hg} present in the tube till that point (obtained by dividing the cumulative mass of mercury added to the tube till the calibration point by the density of the mercury at the temperature when heights were measured) the volume of the mercury meniscus complement (V_C)



h_m = Height of meniscus.

h = Height in which column was confined from the outside edge of the sealed end.

V_c = Volume (mercury meniscus complement).

V_L = Level volume.

Fig. A - Experimental tube calibration.

$$\text{Letting } V_{\text{Hg}} - \frac{\pi h_m^3}{6} = Y$$

$$\text{and } h - \frac{h_m}{2} = X$$

$$Y = a + bX$$

For each calibration point, Y and X were calculated and a linear equation was fitted for Y in X by means of least squares analysis on the computer. The values of X, Y from the data taken, the values of Y from regression analysis (Y'), the standard deviation in Y along with the constants 'a' and 'b' are given in table (A1). Since the experimental tube used consisted of two precision bored tubes of different sizes two sets of a and b were obtained.

Finally if h is the distance between the closed tip and the upper meniscus of the mercury level in the experimental tube in inverted position, and h_m is the height of mercury meniscus (Figure 13), volume of the sample is given by the following expressions:

(i) for $h < 8$ cm.

$$V = -0.083700 + 0.316900 (h + h_m/2) - \frac{\pi}{6} \times h_m^3$$

(ii) for $12 < h < 45$ cm.

$$V = -1.982260 + 0.50262075 (h + h_m/2) - \frac{\pi}{6} h_m^3$$

The values of V for $8 < h < 12$ are obtained by using the spline fit whenever necessary.

TABLE A1CALIBRATION OF EXPERIMENTAL TUBE

Sl. No.	X in cm.	Y in cc.	Y' in cc	Error in Y in cc (Y-Y')
---------	-------------	-------------	-------------	----------------------------

Upper Portion

1.	1.1922	0.2969	0.2941	0.0028
2.	1.8792	0.5096	0.5118	0.0022
3.	3.0638	0.8866	0.8872	0.0006
4.	4.4308	1.3204	1.3204	0.0000
5.	6.1210	1.8549	1.8560	0.0011
6.	8.4222	2.5864	2.5853	0.0011

Standard deviation () = 0.0020

a = -0.083700

b = 0.316900

Middle Portion

1.	15.7822	5.9456	5.9501	0.0045
2.	22.3794	9.2656	9.2660	0.0004
3.	25.8156	10.9932	10.9931	-0.0000
4.	30.9390	13.5769	13.5682	-0.0086
5.	34.4146	15.3217	15.3152	-0.0064
6.	37.2341	16.7292	16.7323	0.0031
7.	39.3054	17.7690	17.7734	0.0043
8.	42.6700	19.4658	19.4645	-0.0011
9.	44.4372	20.3489	20.3527	0.3859

Standard deviation () = 0.0051

a = -1.98226

b = 0.50262

APPENDIX 'B'

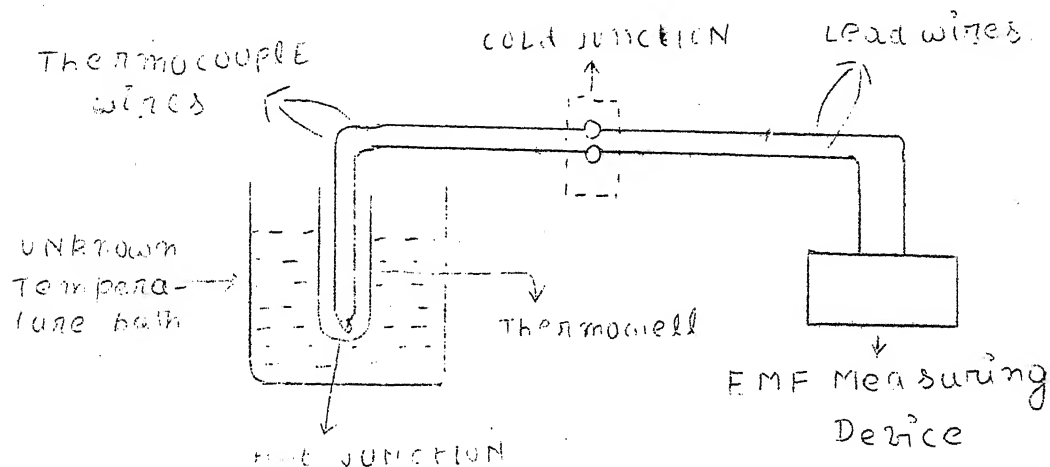
THERMOCOUPLE CALIBRATION

For temperature measurements in thermodynamic studies, thermocouple is a fairly accurate and stable measuring device with rapid response and low maintenance cost. Commonest thermocouples are chromel-alumel, iron-constantan, copper-constantan etc., and their selection depends upon various factors like range of temperature measurements needed, types of atmosphere surrounding the measuring junction etc. For the present work ~~copper-constantan~~ Thermocouple has been chosen.

Measurement of temperature by means of thermocouple is based on the simple fact that when two junctions formed by two dissimilar metals are maintained at different temperatures, depending upon the temperature difference between the junctions, small electromotive force is generated in the circuit. Every thermocouple bears certain relationship between the temperature difference of the two junctions and the electromotive force developed in the circuit.

One of the junctions, called cold junction (or Reference junction) is maintained at a known temperature (usually ice point), and the other junction, known as hot junction, is inserted into the unknown temperature bath.

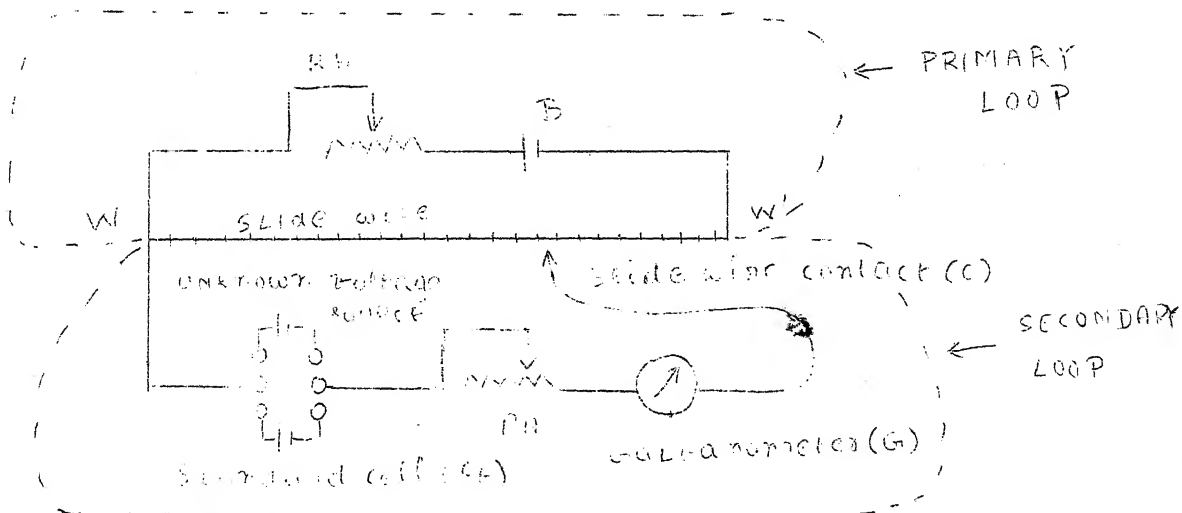
The electromotive force generated in the circuit is measured by a milli voltmeter. By making use of the relationship between the temperature difference of the two junctions and the EMF developed in the particular thermocouple, the unknown temperature is calculated. A simple thermocouple circuit is shown below:



The relationship that the thermocouple bears on the EMF generated depends not solely on the type of metals used, but on the way in which the junctions are made and the type of lead wires used for connecting the thermocouple to the EMF measuring device as well. So, in order to make use of the thermocouple circuit for measuring unknown temperature it is necessary to calibrate the thermocouple with particular junctions and lead wires in the circuit against some standard instrument. In the present work the thermocouple was calibrated against a standard platinum Resistance Thermometer (Leeds & Northrup Company). Mueller's bridge, also of

Leeds & Northrup Company was used to measure the Resistance of the platinum Resistance Thermometer. The resistance of the platinum resistance thermometer bears a certain relationship with the temperature surrounding the element of Platinum Resistance Thermometer. This relation in the form of charts and a mathematical formula is supplied along with the Resistance Thermometer.

The millivolts developed in the thermocouple circuits are measured by means of Potentiometers. Potentiometers have advantage over the other types of EMF measuring devices in the fact that they draw no current from the source of unknown voltage when the circuit is balanced for EMF measurement. In potentiometers unknown voltage is balanced against a known potential drop. This known potential drop is due to the flow of current through some standard resistances. A simplified potentiometer circuit is given below.



Essentially, the circuit comprises of two loops - a primary loop and a secondary loop. At the balancing condition no current flows in the secondary loop. The secondary loop consists of either a standard cell or the unknown voltage source at a time along with a null detector (G), a high Resistance Rheostat 'PA' and a slide wire contact (C). Null detector is for checking the balancing condition in the secondary loop. Rheostat 'PA' is to control the current flow in the secondary loop before balancing condition is obtained so as not to allow more than one milli ampere in the secondary loop when standard cell is in the circuit. The calibrated slide wire WW' has uniform resistance throughout its length, whose Resistance per unit length is known. The primary loop has voltage source (a Battery 'B') and a Rheostat 'RH'. 'B' is the current source for flow of current through the slide wire WW'. When balancing condition is obtained. 'RH' is to adjust the potential drop across the slide wire to make equal to the voltage of the standard cell 'St'. Standard Cell supplies a constant current at a constant voltage for a long time and is used to standardize the current in the slide wire WW'. The working procedure of the potentiometer is briefly given below.

Slide wire contact 'C' is placed at its extreme right position. PA is kept at its highest resistance (e.g. 1000-) and the switch 'S' is operated so as to connect the Standard Cell 'St' in the secondary circuit. Rheostat 'RH' in the primary circuit is adjusted such that galvanometer (G) indicates zero. Now PA is slowly decreased in small steps, so that not more than one mill ampere flows through the secondary loop (standard cell) so as to protect the standard cell, and at each step RH is adjusted for zero reading of the galvanometer (balancing the circuit). All the time slide wire contact 'C' is undisturbed from its extreme right position. Finally when PA is zero and the bridge is balanced, the potential drop across the full length of the slide wire is exactly equal to the EMF of the standard cell, which is known accurately. In this balanced condition the slide wire draws a current I_s from the Battery 'B'.

($= \text{EMF of 'St' / Resistance of full slide wire } R$). Now without disturbing 'RH' and 'PA' (which is at zero resistance) the unknown voltage is connected in the secondary loop and the bridge is balanced by adjusting the slide wire contact 'C' alone. At the balancing condition unknown voltage is equal to the potential drop across the slide wire in the secondary circuit through which the current, same in value as I_s , is flowing again. So the unknown voltage is equal to product of I_s and the Resistance of slide wire (R) between 'W' and

'C'. 'R' is obtained by measuring the length of the slide wire 'WC' and multiplying it by the Resistance per unit of slide wire.

In the present work Honeywell's K-1 potentiometer was used. It has two measuring ranges - one from 0 to 10 millivolts with fourth decimal place being estimated by eye, and the other from 0 to 100 millivolts with third decimal place being estimated by eye. With this potentiometer temperature differences as small as 0.01°C in the working range of temperatures can be detected.

Mueller's bridge is nothing but an improvement of the basic Wheatstone bridge to facilitate very accurate Resistance measurements. The one used in the present work is that of Leeds & Northrup Company and has a high resistance range and three low resistance ranges. The latter has again three resistance measuring ranges enabling it to be used with thermometers having low (0.25 - 1.00 ohm), intermediate (10-100 ohms) or high (greater than 1000 ohms) resistance values at 0°C . In the intermediate range, resistance values are exactly reproducible to the fourth decimal place. The platinum resistance thermometer used in the present work has a reported resistance of 25.554216 ohms at 0°C . So the intermediate range is chosen for the present work. The Mueller's bridge has a built-in galvanometer for null detection when the circuit is balanced. But this

needs a Battery of 8.48 volts exact. Since the battery to this requirement was not available an external Leeds and Northrup galvanometer is used with the bridge for null detection.

Thermocouple was calibrated against the platinum resistance thermometer in a constant temperature vapour bath. The schematic diagram of this apparatus is given in Figure 14. The principal part of this apparatus is the Vapour Jacket 'VJ'. In the side arm flask of 'VJ' a pure liquid is taken and boiled at a constant total pressure in a Nitrogen (inert) atmosphere. The vapours will condense in the condenser 'CD' and are recirculated back to the side arm flask. The principle behind this is due to the fact that a pure substance boils at a constant temperature when the total pressure is fixed. In order to dampen the pressure fluctuation, thereby temperature fluctuations, the volume of the system was increased by connecting two 20 liter flasks (Ballasts) to the system. The temperature inside the vapour jacket can be varied by changing the Nitrogen pressure in the system. Changes in the nitrogen pressure of the system can be affected by the vacuum pump 'MP' and high pressure nitrogen cylinder with a low pressure regulator connected to the system. The vapor jacket has a glass cap at its top which carries two thermowells in the vapour jacket. Plantinum resistance thermometer is inserted into one of the

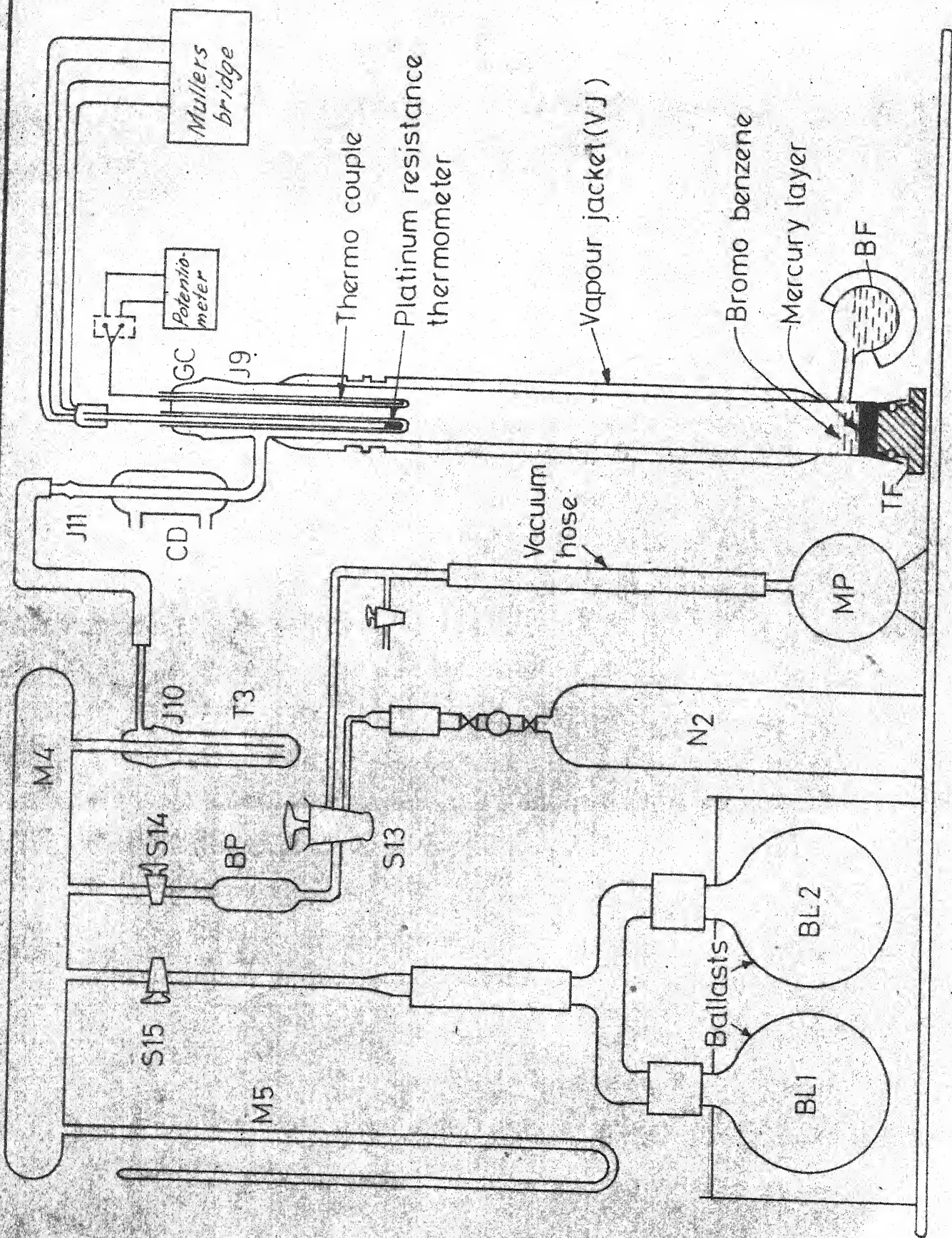


Fig. B - Calibration of thermocouple.

thermowells. Since the platinum resistance thermometer was calibrated by the U.S. National Bureau of Standards with 7" depth of immersion, same depth has been kept under silicone oil in the thermowell. The hot junction of the thermocouple is inserted into the other thermowell. The bottom of the vapour jacket is plugged by means of a Teflon plug with an O-ring outside. Mercury is poured onto this plug so as to prevent O-ring from being attacked by the chemical used in the vapour jacket as well as to prevent leakage through this joint. Bromo benzene has been used for calibration from 100°C-155°C (corresponding to 100 mm of Hg to 760 mm of Hg).

The cold junction of the thermocouple is maintained at the ice point. For this purpose ice bath is made out of crushed ice and distilled water in a thermoflask. Ice is added from time to time and the ice plus water slurry stirred thoroughly with a glass rod in order to ensure its saturation temperature at 0°C. The cold junction of the thermocouple is inserted into this bath. A mercury thermometer is also inserted into this bath to check the constancy of temperature in this bath.

The resistance-temperature relationship for the platinum resistance thermometer is given by the Callender's equation below.

$$\begin{aligned}
 t' &= \frac{100(R_t - R_0)}{R_{100} - R_0} + \delta \left(\frac{t'}{100} - 1 \right) \frac{t'}{100} \\
 &= \frac{1}{\alpha} \left(\frac{R_t}{R_0} - 1 \right) + \delta \left(\frac{t'}{100} - 1 \right) \left(\frac{t'}{100} \right)
 \end{aligned}$$

An alternate form which is completely equivalent to the above is

$$R_t = R_0 (1 + At' + B t'^2)$$

where $A = \alpha (1 + \delta / 100)$

$$B = -\alpha \delta / 10^4$$

The platinum resistance thermometer used in the present work was calibrated by U.S. National Bureau of Standards and their reported values of the constants in Callenders equation are given below:

$$R_0 \text{ (Resistance at ice point)} = 25.5814 \, \Omega$$

$$\text{(Fundamental Coefficient of Coil)} = 0.003926833$$

$$\delta = 1.496176$$

Before using the platinum resistance thermometer, it is checked for the ice point with Mueller's bridge. It gave a value in agreement with the reported value within $\pm 0.0001 \, \Omega$.

Using the above formula and constants, a table is generated with the help of a computer to give the Resistance value of platinum resistance thermometer at 0.005°C of temperature intervals from 0°C to 300°C . This table can be used to read directly the temperature from the resistance

of platinum resistance thermometer.

It is observed that the resistance measurement by Mueller's bridge is very accurate and correspondingly the accuracy of temperature measurement is better than $\pm .001^{\circ}\text{C}$. But there may be some uncertainty with the potentiometer readings. So it is decided to treat temperature as the independent variable which can be taken as exact and millivolts of potentiometer reading as dependent variable in finding out the mathematical relation between these two quantities. The data on millivolts vs temperature were subjected to the least squares polynomial regression analysis along with F-static to test the goodness of the fit. It is observed that first degree polynomial with standard deviation in millivolt equal to .0581 fit the data statistically the best. The constants of the polynomial are given in Table B1 with results.

A table similar to the one for platinum resistance thermometer, is generated by means of computer to read the millivolts of potentiometer, that corresponds to a particular temperature at intervals of 0.01°C .

Constants are : $A = -0.62194239$

$B = 0.048964808$

Milli volts $= A + B \times T$

TABLE B1CALIBRATION OF THERMOCOUPLE

Sl. No.	Resistance of Platinum resistance thermometer	Corresponding temperature, °C	Milli volts of Potentio-meter, M.V.	Millivolts from Polynomial Regression
1.	32.9727	73.2851	3.0315	2.9664
2.	35.1008	94.6820	3.9900	4.0141
3.	37.1285	115.2115	4.9625	5.0195
4.	38.6313	130.5032	5.7100	5.7681
5.	39.9276	143.7510	6.3580	6.4167
6.	40.2232	146.7824	6.5065	6.5652
7.	40.5255	149.8821	6.6600	6.7170

Standard deviation = 0.0588

Milli volts = $A + B \times T$

A = -0.62194239

B = 0.048964808

APPENDIC C

CALIBRATION OF PRESSURE GAUZE

The precision bourdan gauze used in the present work (0-300 psia range) is Seegers Instruments Company's standard test gauze. It was checked for calibration against Ruska Instrument Corporation's standard dead weight gauze. The readings obtained are shown in Table C1. The readings agree to better than 0.1 psi for the above pressure gauze which is smaller than the smallest division 0.2 psi of the gauze. The error in readings are random and so no further corrections were applied for the pressure gauze and the readings were accepted as they are shown by it.

TABLE C1CALIBRATION OF PRESSURE GAUZE

Sl. No.	Pressure gauze read ing	Dead weight gauze reading	error
1.	280.00	279.93884	-0.06116
2.	258.50	258.48009	-0.01991
3.	240.40	240.34420	-0.0558†
4.	220.10	220.10567	0.00567
5.	200.30	200.36786	0.06785
6.	180.20	180.26219	0.06219
7.	160.20	160.14364	-0.05636
8.	140.80	140.79325	-0.00675
9.	100.20	100.22054	0.02054
10.	80.10	80.12137	0.02137
11.	60.70	60.71150	0.01150

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